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MINTEQA1, an Equilibrium Metal Speciation Model User's Manual

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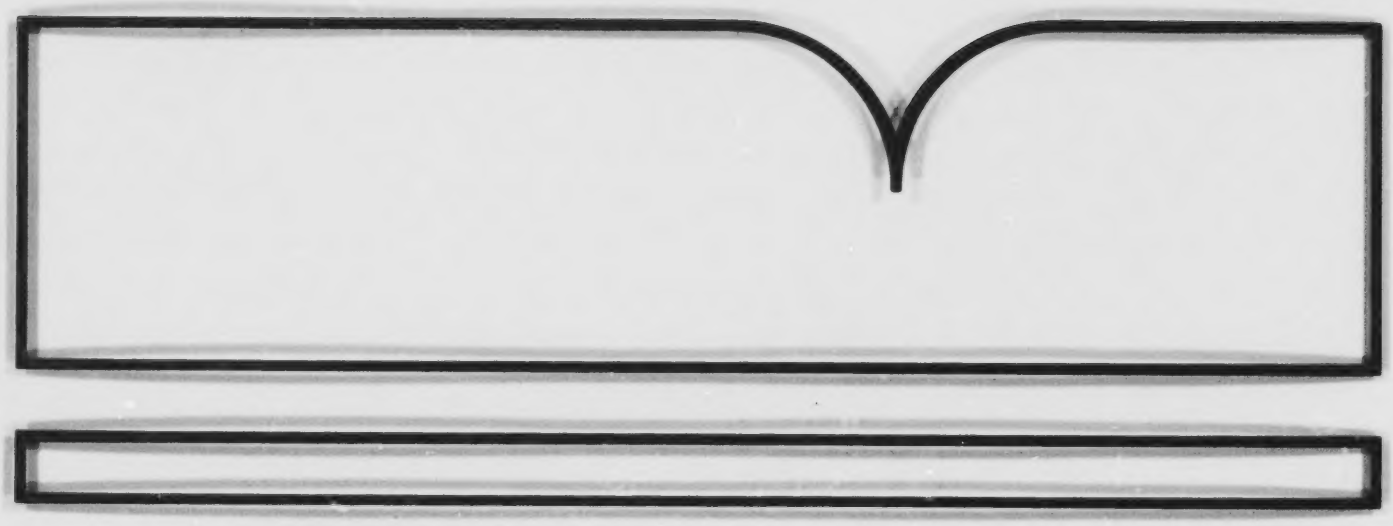

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User's Manual

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by

David S. Brown and Jerry D. Allison+

Assessment Branch
Environmental Research Laboratory
Athens, Georgia 30613

+Computer Sciences Corporation
Environmental Research Laboratory
Athens, Georgia 30613

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ATHENS, GEORGIA 30613

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FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient management tools based on greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement, transformation, impact and control of environmental contaminants, the Assessment Branch develops management or engineering tools to help pollution control officials achieve water quality goals.

The attention of environmental decision makers is increasingly being focused on the movement of pollutants into ground water. Of particular importance is the transport and speciation of metals. The MINTEQA1 model is a versatile, quantitative tool for predicting the equilibrium behavior of metals in a variety of chemical environments. Designed for convenient use by environmental scientists and engineers, the model should be a valuable tool for environmental risk assessment and hazard evaluation.

Rosemarie C. Russo, Ph.D.
Director
Environmental Research Laboratory
Athens, Georgia

ABSTRACT

Recent advances in technical understanding of the processes controlling the behavior of pollutants in the environment have led to the development of many predictive models. MINTEQA1 is a versatile, quantitative geochemical model for predicting the equilibrium behavior of metals in a variety of chemical environments. The complex series of reactions among solution species, gases, solids, and sorbed phases can be modeled relatively easily using MINTEQA1. This MINTEQA1 manual is designed to acquaint new users with the geochemical principles and mathematical formalisms involved in using the program. A major goal is to minimize the effort unfamiliar users must expend in acquiring an operational knowledge of this valuable environmental modeling tool and thus promote its use in a variety of environmental risk assessment and hazard evaluation scenarios. To facilitate this goal, an interactive preprocessor program PRODEFA1 also is discussed. PRODEFA1 assists new users by assembling the sometimes complicated MINTEQA1 input files automatically in response to an on-line question and answer dialogue that places minimal demands on potential new users. Using PRODEFA1, environmental scientists and engineers can rapidly learn to extract many of the benefits of MINTEQA1 without the initial complication of having to simultaneously learn input file formatting details.

This report covers the period from April 1, 1986 to March 31, 1987 and work was completed as of February 1, 1987.

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CHAPTER 1

INTRODUCTION

Technical understanding of the physical, chemical, and biological processes controlling the behavior of pollutants in the environment has increased significantly in the past two decades. Many of the important advances are reflected in the quantitative mathematical models now being used to describe the influences of competing processes or reactions on the overall behavior of pollutants. A variety of mathematical models encompassing years of research are now available for predicting behavior of pollutants in various environmental settings. The metal speciation model, MINTEQA1, described in this manual is a versatile, state-of-the-art example of the equilibrium solution chemistry programs now available. The MINTEQA1 program is designed to solve a broad range of complex chemical equilibrium problems involving reactions among gases, aqueous solutions, mineral phases, and adsorbed phase species with minimal demands on the user.

Included in MINTEQA1 is an extensive thermodynamic database that is adequate for solving a broad range of problems without need for additional user-supplied information. The standard database can be easily modified, however, if it is found to be incomplete or inadequate for a particular problem. Thermodynamic data are not included for any of the optional sorption algorithms available in the program. The state-of-the-art in metal sorption research has not yet progressed to the point that thermodynamic equations of state are available to define the complex array of competitive metal sorption reactions expected to occur in various environmental situations.

The empirical nature of the available metal sorption data reflects the fact that natural sorbent phases often occur as mixtures of impure, ill-defined, interacting amorphous mineral and organic components that vary widely in chemical behavior from site to site. For this reason, sorption data are left to the discretion and problem-specific knowledge of the user. Six sorption models are available in MINTEQA1 to match the quality and type of metal sorption data available for specific problems.

An optional preprocessor program PRODEFA1, is included to assist unfamiliar users in assembling the complex input files that are sometimes required. PRODEFA1 is an interactive preprocessor designed to lead new users through a standard set of questions necessary to formally define the desired chemistry problem in MINTEQA1 format. The use of PRODEFA1 frees users of the distractions of learning component identification numbers and formatting details. PRODEFA1 provides a liberal menu of optional help texts to assist in learning MINTEQA1 formalisms, reviewing chemical concepts, or developing appropriate responses to the interactive questions.

Error recovery options are provided to allow partially completed input files (and the interactive dialogue text) to be recalled and to allow completed files to be checked and edited. A number of checks also are incorporated to warn users of impending convergence failure resulting from improper, incomplete, or over-restrictive specification of the problem being defined.

CHAPTER 2

PURPOSE

The purposes of this manual are manifold. One objective is to provide new MINTEQA1 users with an outline of the many chemical and geological principles that control chemical equilibria among electrolyte solutions, gases, and solid phases. The treatment provided is not rigorous, however, and is intended only as a brief review. Most of the basic chemical concepts encompassed by MINTEQA1 are well documented elsewhere.

The more difficult aspect of comprehending chemical equilibria is to gain a "feel" for the complex and extensive ways these rather simple concepts interact to determine the position of final equilibrium in solutions containing many components. Often, it is confusion about this latter issue that limits progress in solving problems that otherwise involve relatively simple concepts. This is also an area where assistance from computers is a welcome and expedient alternative.

Many users will find that the greatest utility of MINTEQA1 (or other chemical equilibrium models) is the assistance provided in isolating the controlling reactions in complex systems. Ironically, these controls are typically quite amenable to desktop evaluation once isolated.

Ultimately, it is the experience gained from operating the model in both successful and unsuccessful execution attempts that leads most quickly to an understanding of the systems under investigation. This philosophy is not offered in support of the blind usage of MINTEQA1 or any other model; rather, it is meant to imply that for complex systems, trial and error may be the best teacher. This manual, together with PRODEFA1, will allow new users to begin this learning process with minimal initial preparation. Extensive text entries are included in PRODEFA1 to facilitate convenient on-line reference along the way. Frequent use of the "help" options in PRODEFA1's questioning routine will provide an element of programmed learning.

Another objective is to familiarize users with the mathematical formalisms used in formulating chemical equilibria problems. This is accomplished using a series of detailed examples representing simple chemical systems likely to be familiar to the user. These examples closely follow the clear, concise development provided by Westall (19).

A final objective is to help users gain experience with MINTEQA1 through modeling a few very simple systems. Example input files are provided for several simple systems to illustrate how various chemical constraints are accommodated in MINTEQA1. These examples will provide useful practice situa-

tions and help users determine whether the programs are properly installed and operational on their equipment.

CHAPTER 3

HISTORY OF MINTEQA1 AND PRODEFA1

The MINTEQA1 equilibrium geochemical model is a late generation addition to the REDEQL (10) family of models which has evolved over a period of more than 15 years. The original version (MINTEQ) was developed at Battelle's Pacific Northwest Laboratory (7) by combining the versatile mathematical formalism from MINEQL (21) and the well-developed thermodynamic data base from the U.S. Geological Survey's WATEQ3 model (1). With the exception of expanded matrix dimensions, minor overrun fixes, and a substantially expanded data base, MINTEQA1 is nearly identical to the original MINTEQ.

Because of the level of detail required to properly specify complex chemical equilibrium problems, the development of input data files is often tedious. This difficulty, coupled with the frustrations of having to learn chemical component and species identification numbers, mathematical formalisms, and formatting details, has deterred many potential users from using chemical equilibrium modeling programs to maximum advantage. To circumvent this problem, a series of preprocessor programs designed to simplify model usage have evolved.

The earliest preprocessor program, MISP (6), was developed at Battelle's Pacific Northwest Laboratory for use with MINTEQ. Lacking efficient error recovery options, MISP was soon abandoned in favor of a much improved version designated PRODEF (12). This new code also was developed at Battelle through funding support from several sources (U.S. Department of Energy, U.S. Environmental Protection Agency, and the Electric Power Research Institute). The present preprocessor program, designated PRODEFA1, is identical to PRODEF in all major respects, but incorporates many modifications and additions to the "help" text entries including an expanded section explaining how to avoid phase rule violations and other errors in formulating the problem. These latter changes were incorporated at the Environmental Research Laboratory, Athens, Georgia, to facilitate rapid on-line reference.

CHAPTER 4

THERMODYNAMIC PRINCIPLES

Several fundamental thermodynamic principles are important in solving geochemical equilibrium problems. This chapter provides a brief review of these relationships with particular emphasis on the mathematical formalisms used in MINTEQA1. For this purpose it is instructive to define several key terms used in the program.

To provide versatility in solving a broad range of problems using a consistent mathematical formulation, several chemical species types are defined in MINTEQA1 and PRODEFA1. There are seven species types in all. Types 1 through 6 are used in MINTEQA1. Type 7 is a special category used only temporarily in PRODEFA1. All Type 7 species are redefined as Types 1 through 4. All species types are defined below. These definitions are also a part of the PRODEFA1 help text.

SPECIES DEFINITIONS

Type 1

COMPONENTS: Basis species or "components" are aqueous species that are chosen from the component database to represent reactants in all reactions to be considered. Only "components" are used to represent reactants in chemical reactions that generate other species as products. Each element in the database is represented by at least one, and frequently several, components. Elements that have more than one important oxidation state must have multiple component species identifiers. For instance, sodium is represented by the single component Na^+, but iron is represented by Fe^{2+} and Fe^{3+} to reflect the two predominent oxidation states.

Many components of the component database were chosen as the simple ions (e.g., Na^+, Fe^{2+}, Fe^{3+}) as opposed to compound species such as H_4SiO_4 and H_3BO_3. Compound species are used where there is a gain in mathematical efficiency in representing the overall chemical equilibria. Ultimately, the components were selected such that all possible species from the thermodynamic database can be produced from a minimum set of components. This results in minimization of the mathematical dimensions of the problem.

A complete listing of the component species available in the MINTEQA1 database is given in Table 4.1. Entering analytical concentrations of the component species is central to setting up a MINTEQA1 modeling exercise and often constitutes the majority of effort in preparing the input data files.

TABLE 4.1. COMPONENT SPECIES CURRENTLY REPRESENTED IN THE MINTEQA1 THERMODYNAMIC DATABASE. THE 3-DIGIT NUMBER IS THE SPECIES ID.

ID Number	Name	ID Number	Name	ID Number	Name	ID Number	Name
001	e^-	150	Ca^{2+}	460	Mg^{2+}	800	Sr^{2+}
002	H_2O	160	Cd^{2+}	470	Mn^{2+}	870	Tl^+
020	Ag^+	180	CL^-	471	Mn^{3+}	871	$Tl(OH)_3$
030	Al^+	210	Cr^{2+}	490	NH_4^+	890	U^{3+}
060	H_3AsO_3	211	$Cr(OH)_2^+$	491	NO_2^-	891	U^{4+}
061	H_3AsO_4	212	CrO_4^{2-}	492	NO_3^-	892	UO_2^+
090	H_3BO_3	220	Cs^+	500	Na^+	893	UO_2^{2+}
100	Ba^{2+}	230	Cu^+	540	Ni^{2+}	900	V^{2+}
130	Br^-	231	CU^{2+}	580	PO_4^{3-}	901	V^{3+}
140	CO_3^{2-}	270	F^-	600	Pb^{2+}	902	VO^{2+}
141	Fulvate	280	Fe^{2+}	680	Rb^+	903	VO_2^+
142	Humate	281	Fe^{3+}	730	HS^-	950	Zn^{2+}
143	Acetate	330	H^+	731	S	990	SOH1
144	Tartrate	360	Hg_2^{2+}	732	SO_4^{2-}	991	SOH2
145	Glycine	361	$Hg(OH)_2$	760	HSe^-	992	XPSIO
146	Salicylate	380	I^-	761	$HSeO_3^-$	993	XPSIB
147	Glutamate	410	K^+	762	SeO_4^{2-}	994	XPSID
148	Phathalate	440	Li^+	770	H_4SiO_4	995	SOHB

Appendix C contains information on species nomenclature and MINTEQA1's thermodynamic database.

Type 2

COMPLEX: A "complex" is formed from the reaction of two or more components. The reaction below illustrates the formation of the Type 2 complex ($NaHCO_3$) from the combination of three components (Na^+, H^+ and CO_3^{2-}).

$$Na^+ + H^+ + CO_3^{2-} \text{ ----> } NaHCO_3 \qquad 4.1$$

Likewise, for a sorption reaction between a surface site component (designated by SOH) and a sodium ion component, the new complex SO-Na is formed.

$$SOH + Na^+ \text{ ----> } SO\text{-}Na^+ + H^+ \qquad 4.2$$

Note that a hydrogen ion component was exchanged in the reaction.

Type 2 complexes are read from the thermodynamic database and need not be entered except in the case of complexes resulting from sorption reactions or reactions not in the database.

Type 3

FIXED SPECIES: A "fixed species" can be any species with a fixed activity. These species are commonly one of four types: 1) components that the user wishes to introduce at a fixed activity, such as H^+ or e^-, 2) solid phases that are present in infinite supply, 3) gases that are present at a fixed partial pressure, and 4) redox reactions between any two components.

Type 4

FINITE MINERAL: A mineral that is initially present in a finite quantity and subject to complete dissolution during the approach to equilibrium.

Type 5

POTENTIAL MINERAL: A "potential mineral" is defined as a solid phase that is not present initially, but which may form during chemical equilibration. If the solubility products are exceeded during the course of reaction (equilibration), potential minerals will precipitate.

Users should introduce Type 5 species judiciously when preparing input data files. Introducing the complete list of all possible solids in a complicated system will greatly, and unnecessarily, complicate the computations. Only those solids that are considered likely to precipitate should be introduced. Ideally, the minimal list of probable solids can be obtained by inspecting the saturation index listings from a pilot model run that purposefully prohibits precipitation.

Type 6

EXCLUDED SPECIES: An "excluded species" is an aqueous component or complex, a mineral, or a gas that is in the thermochemical database, but is excluded from the mass balance calculations. Examples are the electron and the adsorption potentials that are treated as components in the constant capacitance and triple-layer adsorption models.

Type 7

ADDED SPECIES: These are always either components or other species that are not present in the thermodynamic database but are needed in the problem. The "other" species include aqueous complexes, gas or solid phases, redox couples, and adsorption products. PRODEFA1 initially designates all added species as Type 7 but re-assigns each one to the appropriate type (1-5) before entering them in the MINTEQA1 input file. MINTEQA1 treats all added species as an addendum to the thermodynamic database.

PROBLEM FORMULATION

Chemical equilibrium problems are normally formulated in one of two ways: 1) minimization of the system free energy under mass balance constraints or 2) simultaneous solution of the nonlinear mass action expressions and linear mass balance relationships. Van Zeggeren and Storey (18) have shown these two approaches to be mathematically equivalent. MINTEQA1 uses the more common, latter approach, also commonly refered to as the "equilibrium constant method". This method also is used in several other geochemical equilibrium programs including PHREEQE (13), EQ3NR (22), and MICROQL II (19).

In the equilibrium constant method, all applicable mass action reactions are written using an arbitrarily selected set of input "components" (Type 1 species) as reactants. The choice of input components is not unique, but the components must be selected such that all species (Type 2, 3, 4, 5) in the system can be generated from reactions among the components. In a properly chosen set, no components can be formed from a reaction among the other components.

Chemical equilibrium problems are formulated in MINTEQA1 by combining all the mass action constraints (equilibrium constant expressions) for reactions among the components with mass balance expressions for each component.

The number of degrees of freedom of the system is the number of independent variables. These would ordinarily include temperature, pressure, and all the component masses that can be independently varied. Several constraints are used in MINTEQA1 that modify the usual phase rule relationship. Because temperature and pressure are both specified invariant by the user (pressure is fixed indirectly by specifying the value of the equilibrium constant appropriate for the partial pressure of the gas phase) the phase rule expression that applies to MINTEQA1 calculations is

$$f = C - P \qquad 4.3$$

Where:

f = the number of degrees of freedom

C = the number of components

P = the number of phases

One additional degree of freedom is lost for each component entered at fixed activity (Type 3 species). In MINTEQA1, the activity of the H_2O component is always fixed at the outset by convention (see Equation 4.34). This simplification saves computation time and does not significantly alter the outcome of calculations performed on relatively low ionic strength solutions. Other components such as pH (H^+) and pe (e^-) are also commonly fixed at various activities selected by the user. In addition to these constraints, MINTEQA1 takes advantage of the phase rule by eliminating one degree of freedom (fixing the concentration of one component) for each solid phase at equilibrium with the solution. This follows from the solubility product constraint imposed by the presence of a solid phase. Consider, for example, the following reaction

$$2Ag^+ + S^{2-} \langle==\rangle Ag_2S \downarrow \qquad 4.4$$

If a pure acanthite phase is present at unit activity,

$$K_{sp} = [Ag^+]^2 \ [S^{2-}] = 10^{-56} \qquad 4.5$$

and $[Ag^+]$ and $[S^{2-}]$ are no longer independent variables.

In the absence of constraints like this, a system containing j components would be represented by a set of j mass action expressions of the form

$$C_i = K_i \prod_j X_j^{a_{ij}} \qquad 4.6$$

Where:

C_i = concentration of species i

K_i = formation constant for species i

X_j = concentration of component j

a_{ij} = stoichiometric coefficient of component j in species i

π = indicates the product over all components in species i

One expression of this form will exist for each species i. Activity coefficients are omitted in Equation 4.6 for simplicity.

In logarithmic form, Equation 4.6 becomes

$$\log C_i = \log K_i + \sum_j a_{ij} \log X_j \qquad 4.7$$

and in matrix form, the system of equations for all species i can be written

$$\log \overline{C} = \log \overline{K} + \overline{A} \log \overline{X} \qquad 4.8$$

Where:

$\log \overline{C}$ = a column vector of $\log C_i$

$\log \overline{K}$ = a column vector of $\log K_i$

$\log \overline{X}$ = a column vector of $\log X_i$

$\overline{A}$ = the matrix of stoichiometric coefficients a_{ij}

In addition to the mass action expressions, the unrestricted system of j components would be governed by j mass balance equations of the form

$$T_j = \sum_i a_{ij} C_i \qquad 4.9$$

Where:

T_j = total system mass of component j

C_i = concentration of each species i

a_{ij} = stoichiometric coefficient of component j in species i

Because MINTEQA1 employs an iterative numerical technique (Newton-Raphson method; see Appendix A) to arrive at the solution, an error term (y_j) is defined such that

$$y_j = \sum_i a_{ij} C_i - T_j \qquad 4.10$$

Where.

y_j = the error, or remainder, in the mass balance equation for each component j

A final solution will be obtained when

$$|y_j| \leq \text{convergence criteria} \qquad 4.11$$

The convergence criteria for MINTEQA1 is pre-set to 0.001.

The goal to find a solution such that y_j converges toward zero. This could be accomplished using a variety of available numeric methods. The Newton-Raphson method is used in MINTEQA1 because it converges rapidly (second order) near the solution. The drawback is that this method sometimes does not converge at all if poor initial estimates of component activities (activity guesses) are provided. The initial activity guesses supplied automatically by PRODEFA1 are set at 1.0 times the total analytical input concentration of each component. If these prove inadequate, users may provide their own guesses. It is sometimes helpful to also select the optional line-search convergence method that is provided in the program. In most cases, convergence will be obtained for properly formulated problems; however, additional suggestions regarding persistent convergence problems are provided as on-line text entries in PRODEFA1.

To illustrate the generalized mathematical formalisms useful for solving chemical equilibrium problems, it is instructive to consider a simple problem in detail. The example problem formulation that follows is based on a simple calcium carbonate ($CaCO_3$) solution. This solution has served as the classical example for many chemical equilibrium models and has been discussed in great detail elsewhere (6, 7, 19). The development that follows is taken largely from these sources and differs only in the specifics relating to MINTEQA1. A 0.001 molar solution of $CaCO_3$ that has no access to atmospheric gases is considered. Because the $CaCO_3$ will dissolve completely in this case, no solid phases are considered. Furthermore, no sorbent phases are present, no redox reactions occur, and no "fixed" species are included.

The $CaCO_3$ solution at equilibrium will contain nine solution species: Ca^{2+}, $CaOH^+$, $CaCO_3$ (aq), $CaHCO_3^+$, H_2CO_3, HCO_3^-, CO_3^{2-}, H^+ and OH^-. The first step in formulating the equilibrium problem is to select a minimum set of "component" species (Type 1 species in MINTEQA1) that will serve as the sole reactants in the set of reactions that yield all the remaining species as products. The "complexes" formed by these reactions are defined as Type 2 species in MINTEQA1. Components are selected such that all the required complexes are formed from reactions among the components. The choice of components to represent a given solution, in general, is not unique; however, the component set used in MINTEQA1 is pre-set (see Table 4.1).

The three components from Table 4.1 that are applicable to the $CaCO_3$ solution are Ca^{2+}, CO_3^{2-}, and H^+. Water is also a component, but it is

treated somewhat differently than the others in that H_2O is presumed to exist at constant activity. This is a good assumption for all dilute solutions because the mass of H_2O present is several orders of magnitude greater than the other components. The small mass of water consumed (or generated) by reactions with other components is justifiably neglected. MINTEQA1 automatically inserts H_2O as a component in all solutions and includes the corresponding activity coefficients in all the mass action expressions. Material balance equations for H_2O are not considered because of the constant activity assumption.

Table 4.2 lists all the species to be considered in the $CaCO_3$ problem. Components (Type 1 species) and their reaction products (Type 2 species) are listed separately to emphasize the important distinction between species types.

The set of reactions that generate Type 2 species from the input components are tabulated in Table 4.3 and the corresponding stoichiometric matrix is presented in Table 4.4.

TABLE 4.2. SPECIES TYPES INVOLVED IN A 0.001 MOLAR $CaCO_3$ SOLUTION

All Species Present	Components (Type 1 species)	Complex Species (Type 2 species)
Ca^{2+}	Ca^{2+}	
$CaOH^+$		$CaOH^+$
$CaHCO_3^+$		$CaHCO_3^+$
$CaCO_3$ (aq)		$CaCO_3$ (aq)
H_2CO_3		H_2CO_3
HCO_3^-		HCO_3^-
CO_3^{2-}	CO_3^{2-}	
H^+	H^+	
OH^-		OH^-
$(H_2O)^*$	$(H_2O)^*$	

*MINTEQA1 always inserts H_2O as an input component having constant activity.

TABLE 4.3. REACTIONS AMONG COMPONENTS TO FORM COMPLEX SPECIES IN A 0.001 MOLAR $CaCO_3$ SOLUTION

Reactions	log K
(1) Ca^{2+} ---> Ca^{2+}	0.0*
(2) $Ca^{2+} + H_2O - H^+$ ---> $CaOH^+$	-12.2
(3) $Ca^{2+} + CO_3^{2-} + H^+$ ---> $CaHCO_3^+$	11.6
(4) $Ca^{2+} + CO_3^{2-}$ ---> $CaCO_3$ (aq)	3.0
(5) $CO_3^{2-} + 2H^+$ ---> H_2CO_3	16.5
(6) $CO_3^{2-} + H^+$ ---> HCO_3	10.2
(7) CO_3^{2-} ---> CO_3^{2-}	0.0*
(8) H^+ ---> H^+	0.0*
(9) $H_2O - H^+$ ---> OH^-	-14.0
(10) H_2O ---> H_2O	0.0*

*These trivial reactions are included only to keep the development in general form.

TABLE 4.4. STOICHIOMETRIC MATRIX REPRESENTING THE 0.001 MOLAR $CaCO_3$ PROBLEM

Species	Components			
	Ca^{2+}	CO_3^{2-}	H^+*	H_2O
Ca^{2+}	1	0	0	0
$CaOH^+$	1	0	-1	1
$CaHCO_3$	1	1	1	0
$CaCO_3$ (aq)	1	1	0	0
H_2CO_3	0	1	2	0
HCO_3^-	0	1	1	0
CO_3^{2-}	0	1	0	0
H^+	0	0	1	0
OH^-	0	0	-1	1
H_2O	0	0	0	1

*Coefficients in the H^+ component column are rationalized using H_2O as the reference. The $CaOH^+$ species contains one less H^+ than water; the H_2CO_3 species has two dissociatable H^+ ions; the OH^- species has one less H^+ than water, etc. Similar results could be obtained from charge balance considerations. For example, the reaction in MINTEQAl for $CaOH^+$ is

$$Ca^{2+} + H_2O - H^+ \text{ <====> } CaOH^+$$

Thus, the stoichiometric matrix element corresponding to the amount of H^+ in $CaOH^+$ is -1. Similarly for H_2CO_3

$$CO_3^{2-} + 2H^+ \text{ <====> } H_2CO_3$$

Thus, the stoichiometric matrix element for the H^+ in H_2CO_3 is +2.

If MINTEQAl's component list had been arranged differently (we have already observed that the component list is not unique) so that O^{-2} were a component, then the reaction for H_2CO_3 in the database might have been:

$$CO_3^{2-} + H_2O - O^{-2} \text{ <====> } H_2CO_3$$

and the stoichiometric matrix element for H^+ involved in H_2CO_3 would be zero.

The set of mass action constraints that apply to the reactions in Table 4.3 are given in Table 4.5. In addition to these, three material balance expressions are required to complete the set of equations that define the $CaCO_3$ system. The material balance expressions are generated by summing the concentrations of all species involving each of the components and equating the resulting sums to the respective analytical input concentrations. The resulting expressions are:

$$T_{Ca^{2+}} = (Ca^{2+}) + (CaOH^{+}) + (CaHCO_3^{+}) + (CaCO_3\ (aq)) = 0.001 \text{ molar} \qquad 4.12$$

$$T_{CO_3^{2-}} = (CaHCO_3^{+}) + (CaCO_3\ (aq)) + (H_2CO_3) + (HCO_3^{-}) + (CO_3^{2-}) = 0.001 \text{ molar} \qquad 4.13$$

$$T_{H^{+}} = -(CaOH^{+}) + (CaHCO_3^{+}) + 2(H_2CO_3) + (HCO_3^{-}) + (H^{+}) - (OH^{-}) = 0.0 \qquad 4.14$$

Where parentheses "( )" denote analytical concentrations.

TABLE 4.5. MASS ACTION EXPRESSIONS APPLICABLE TO THE $CaCO_3$ SOLUTION EQUILIBRIUM*

(1) $[Ca^{2+}]\ K_1 = [Ca^{2+}]$	$K_1 = 1$
(2) $[Ca^{2+}]\ [H^{+}]^{-1}\ K_2 = [CaOH^{+}]$	$K_2 = 10^{-12.6}$
(3) $[Ca^{2+}]\ [CO_3^{2-}]\ [H^{+}]\ [H_2O]\ K_3 = [CaHCO_3^{+}]$	$K_3 = 10^{11.3}$
(4) $[Ca^{2+}]\ [CO_3^{2-}]\ K_4 = [CaCO_3\ (aq)]$	$K_4 = 10^{3.2}$
(5) $[CO_3^{2-}]\ [H^{+}]^2\ K_5 = [H_2CO_3]$	$K_5 = 10^{16.5}$
(6) $[CO_3^{2-}]\ [H^{+}]\ K_6 = [HCO_3^{-}]$	$K_6 = 10^{10.3}$
(7) $[CO_3^{2-}]\ K_7 = [CO_3^{2-}]$	$K_7 = 1$
(8) $[H^{+}]\ K_8 = [H^{+}]$	$K_8 = 1$
(9) $[H_2O]\ [H^{+}]^{-1}\ K_9 = [OH^{-}]$	$K_9 = 10^{-14.0}$
(10) $[H_2O]\ K_{10} = [H_2O]$	$K_{10} = 1$

*Brackets "[ ]" denote activities.

The ultimate goal is to solve these material balance expressions under the constraints of the mass action equations in Table 4.5. To do this, the concentration terms in Equation 4.12 through 4.14 must first be re-expressed in terms of activities. Solution of the resulting mass balance equations would yield the equilibrium solution activities of each component species. The component activities would then be used to calculate the equilibrium solution activities of each Type 2 species using the mass action expressions in Table 4.5.

Each concentration term appearing in Equations 4.12 through 4.14 can be expressed in terms of the corresponding species activity by incorporating the appropriate activity coefficients (γ). For the four input components the conversions are:

$$(Ca^{2+}) = \frac{[Ca^{2+}]}{\gamma_{Ca^{2+}}} \qquad 4.15$$

$$(CO_3^{2-}) = \frac{[CO_3^{2-}]}{\gamma_{CO_3^{2-}}} \qquad 4.16$$

$$(H^+) = \frac{[H^+]}{\gamma_{H^+}} \qquad 4.17$$

$$(H_2O) = \frac{[H_2O]}{\gamma_{H_2O}} \qquad 4.18$$

Where the parentheses "( )" denote concentrations and the brackets "[ ]" denote activities.

For the remaining six derived species, the mass action expressions also are incorporated and the resulting expressions are:

$$(CaOH^+) = \frac{K_2\ [Ca^{2+}]\ [H_2O]}{\gamma_{CaOH^+}\ [H^+]} \qquad 4.19$$

$$(CaHCO_3^+) = \frac{K_3\ [Ca^{2+}]\ [H^+]\ [CO_3^{2-}]}{\gamma_{CaHCO_3^+}} \qquad 4.20$$

$$(CaCO_3) = \frac{K_4\ [Ca^{2+}]\ [CO_3^{2-}]}{\gamma_{CaCO_3}} \qquad 4.21$$

$$(H_2CO_3) = \frac{K_5\ [H^+]^2\ [CO_3^{2-}]}{\gamma_{H_2CO_3}} \qquad 4.22$$

$$(HCO_3^-) = \frac{K_6\ [H^+]\ [CO_3^{2-}]}{\gamma_{HCO_3^-}} \qquad 4.23$$

$$(OH^-) = \frac{K_9\ [H_2O]}{\gamma_{H^+}\ [H^+]} \qquad 4.24$$

The material balance equations that MINTEQA1 will solve result from substituting these expressions for the concentration terms in Equations 4.12 through 4.14. The final set of material balance equations then becomes:

$$T_{Ca^{2+}} = \frac{[Ca^{2+}]}{\gamma_{Ca^{2+}}} + \frac{K_2\ [Ca^{2+}]\ [H_2O]}{\gamma_{CaOH^+}\ [H^+]} + \frac{K_3\ [Ca^{2+}]\ [H^+]\ [CO_3^{2-}]}{\gamma_{CaHCO_3^+}}$$

$$+ \frac{K_4\ [Ca^{2+}]\ [CO_3^{2-}]}{\gamma_{CaCO_3}} = 0.001 \qquad 4.25$$

$$T_{CO_3^{2-}} = \frac{K_3\ [Ca^{2+}]\ [H^+]\ (CO_3^{2-}]}{\gamma_{CaHCO_3^+}} + \frac{K_4\ [Ca^{2+}]\ [CO_3^{2-}]}{\gamma_{CaCO_3}} + \frac{K_5\ [H^+]^2\ [CO_3^{2-}]}{\gamma_{H_2CO_3}}$$

$$+ \frac{K_6\ [H^+]\ [CO_3^{2-}]}{\gamma_{HCO_3^-}} + \frac{[CO_3^{2-}]}{\gamma CO_3^{2-}} = 0.001 \qquad 4.26$$

$$T_{H^+} = \frac{-K_2\ [H_2O]\ [Ca^{2+}]}{\gamma_{CaOH^+}\ [H^+]} + \frac{K_3\ [Ca^{2+}]\ [H^+]\ [CO_3^{2-}]}{\gamma_{CaHCO_3^+}} + \frac{2K_5\ [H^+]^2\ [CO_3^{2-}]}{\gamma_{H_2CO_3}}$$

$$+ \frac{K_6\ [H^+]\ [CO_3^{2-}]}{\gamma_{HCO_3^-}} + \frac{[H^+]}{\gamma_{H^+}} - \frac{K_9\ [H_2O]}{\gamma_{OH^-}\ [H^+]} = 0.000 \qquad 4.27$$

Equations 4.25 through 4.27 now contain only equilibrium constants, activity coefficients, component activity terms, and analytical input concentrations. The analytical input concentrations ($^{T}Ca^{2+}$, $^{T}CO_3^{2-}$, and $^{T}H^{+}$) are supplied by the user when the problem is specified. A solution is desired for the equilibrium component activities, from which the activities of all derived species can be calculated using the mass action expressions in Table 4.5. A material balance equation for the informal component H_2O is not included. The mass of water present is always several orders of magnitude greater than the other components and the mass lost due to reactions is insignificant. Inclusion of the material balance equation would be superfluous.

Adjustments to Equilibrium Constants

The equilibrium constants in Equations 4.25 through 4.27 are functions of the system temperature, but the values supplied in MINTEQA1's thermodynamic database are referenced to 25°C and an ionic strength of zero. If the temperature is not at 25°C, a new set of equilibrium constants must be calculated before solving the equations. Also, the activity coefficients are functions of ionic strength and must be adjusted each time species activities are varied during the Newton-Raphson iterations.

Equilibrium Constant Temperature Corrections

MINTEQA1 incorporates two schemes for adjusting the equilibrium constants for temperature. If the necessary data are available in the thermodynamic database, MINTEQA1 uses a power function of the form

$$\log K_T = A + BT + C/T + D\ \mathrm{Log}(T) + ET^2 + F/T^2 + GT^{1/2} \qquad 4.28$$

Where:

T = temperature (K°), and

A - G = empirical constants stored in the thermodynamic database

Only 25 of the 982 species in the database have these constants available.

For any species that does not have the constants needed for equation 4.28, the equilibrium constant associated with that species in the thermodynamic database is corrected for temperature variations from 25°C by the Van't Hoff equation

$$\log K_T = \log K_{T_r} - \frac{\Delta H_r^{\circ}}{2.303\ R}\left(\frac{1}{T} - \frac{1}{T_r}\right) \qquad 4.29$$

Where:

T_r = the reference temperature, 298.16°K

$\log K_{T_r}$ = logarithm of the equilibrium constant at the reference temperature

R = the gas constant

T = the desired system temperature, °K

ΔH_r° = standard enthalpy change at the reference temperature

Caution should be used in attempting to apply MINTEQA1 to high temperature systems. The Van't Hoff equation implicitly assumes the enthalpies of reaction to be independent of temperature. This assumption is not strictly true and significant errors can result at temperatures far above 25°C. For this reason, MINTEQA1 calculations should be restricted to a temperature range below 100°C and applications to high temperature geothermal systems should definitely not be attempted unless empirical temperature correction data are available.

If the standard enthalpy change is not available in the database, MINTEQA1 uses the uncorrected log K's (25°C). Users are encouraged to become familiar with the database and to evaluate the impacts of these limitations on their systems. Missing enthalpy data can be permanently added to the database or, alternatively, temporarily entered into a given model execution using instructions provided by PRODEFA1. The latter option is convenient for testing a given system's sensitivity for individual reaction enthalpies.

Activity Coefficient Corrections

Activity coefficients for all species are functions of solution ionic strength (I) and vary as species distributions alter the ionic strength. During the iterative solution, successive sets of activity coefficients are calculated for all solution species. These are used to generate corrected values of the equilibrium constants that appear in the material balance expressions being solved. During successive MINTEQA1 iterations, activity coefficients are calculated in the subroutine ACTVTY and the corrected equilibrium constants are generated in the subroutine KCORR.

Initial estimates (activity guesses) of the input component activities are provided in the input file for a given problem. Users may enter their own values or default to the preset values provided in MINTEQA1. As a default, the initial activity guesses for each component are equal to the respective analytical input concentrations divided by 100. Users should be aware, however, that PRODEFA1 will automatically insert activity guesses equal to the analytical input concentrations. The MINTEQA1 default is overriden for input files developed by PRODEFA1.

These initial component activity guesses are used to "crudely" estimate the concentrations of each complex species so that the solution ionic strength can be calculated. The solution ionic strength is then used in either the extended Debye-Huckel equation (17) or the Davies equation (3) to calculate activity coefficients (γ) for all charged species. This latter process is repeated for each successive iteration step. Successive sets of γ's are used to derive new log K's from

$$\text{New log } K = \text{Old log } K - \log \gamma.$$

The Debye-Huckel expression used to calculate the activity coefficients is

$$\log \gamma_i = \frac{-A_d \, z_i^2 \, I^{1/2}}{1 + B_d \, a_i \, I^{1/2}} + b_i \, I \qquad 4.30$$

Where:

A_d and B_d = constants that depend on the dielectric constant and temperature

Z_i = the charge on each species i

a_i = ion size parameter

b_i = ion specific parameter that accounts for the decrease in solvent concentration in concentrated solutions

I = solution ionic strength

The ionic strength (I) is calculated from

$$I = \frac{1}{2} \sum_{i=1}^{n} z_i^2 \, C_i \qquad 4.31$$

Where:

C_i = concentration of ion species i

n = number of ion species present in the solution

Z_i = charge on species i

The Debye-Huckel relation above is used only when the parameters a_i and b_i are available in the database. The current database contains a_i and b_i parameters for many major inorganic ion species and a few important trace metals. The values used were taken largely from the WATEQ3 data compilation (1). Where data are not available, MINTEQA1 uses the Davies equation

$$\log \gamma_i = -AZ_i^2 \left(\left[\frac{I^{1/2}}{1+I^{1/2}} \right] - 0.3I \right) \qquad 4.32$$

in which the variables are defined as in Equation 4.30.

With the exception of H_2O, activity coefficients of neutral species are calculated using the development of Helgeson (9),

$$\log \gamma_i = \alpha_1 I \qquad 4.33$$

where the constant α_1 is set equal to 0.1 in MINTEQA1.

Users are cautioned that the activity correction models presented here are not intended for use at ionic strengths greater than 0.5. At higher ionic strengths, users should consider adding expanded versions of the Debye-Huckel equation, which include terms to account for ion interactions occuring in more concentrated solutions. The work of Pitzer and coworkers (14-16) provides some useful alternative equations.

The activity of water is estimated from

$$[H_2O] = 1 - 0.017 \sum_{i=1}^{n} C_i \qquad 4.34$$

where the C_i's represent the concentrations of individual ion species. Equation 4.34 is applicable only in dilute solutions and is based on a derivation using Raoults' law. The proportionality constant (0.017) is derived from a plot of H_2O activity versus the number of solute ions (8).

Successive sets of log K values that reflect the temperature corrections (Van't Hoff) and activity coefficient corrections (Debye-Huckel or Davies) above are computed in subroutine KCORR and substituted into the mass balance expressions. If no solids are specified, the Jacobian matrix relating changes in mass balance to changes in component activities is used to calculate that set of component activities that will simultaneously minimize the mass imbalance for all species. The procedure used is iterative Gaussian elimination and back substitution with a convergence test following each iteration.

In systems containing solids, the material balance equations are further altered before the new set of activities are determined. Assume, for instance, that the example $CaCO_3$ system described earlier was placed in contact with a very large excess of $CaCO_3$ solid phase. This situation might arise if the carbonate solution was flowing through a fractured limestone aquifer matrix material. This new system would be modeled by including a fixed solid phase

(Type 3 species) of calcite. The calcite solubility product constraint would then be imposed and one degree of freedom would be lost. Stated differently, the free carbonate ion activity would no longer be an independent variable because of the following reaction and corresponding Ksp relationship.

$$Ca^{2+} + CO_3^{2-} \longrightarrow \underset{\text{(calcite)}}{CaCO_3 \downarrow} \qquad 4.35$$

$$[Ca^{2+}]\ [CO_3^{2-}] = \text{constant} = Ksp\ \text{(calcite)} \qquad 4.36$$

The free carbonate ion activity would be expressed as

$$[CO_3^{2-}] = \frac{1}{Ksp\ [Ca^{2+}]} \qquad 4.37$$

and eliminated from the mass balance expressions (Equations 4.25 through 4.27) by substitution. After doing this, the new mass balance equations would become

$$T_{Ca^{2+}} = \frac{[Ca^{2+}]}{\gamma_{Ca^{2+}}} + \frac{K_2\ [Ca^{2+}]\ [H_2O]}{\gamma_{CaOH^+}\ [H^+]} + \frac{K_3\ [Ca^{2+}]\ [H^+]}{\gamma_{CaHCO_3^+}\ Ksp\ [Ca^{2+}]}$$

$$+ \frac{K_4}{\gamma_{CaCO_3}\ Ksp} = 0.001 \qquad 4.38$$

$$T_{CO_3^{2-}} = \frac{K_3\ [H^+]}{\gamma_{CaHCO_3^+}\ Ksp} + \frac{K_4}{\gamma_{CaCO_3}\ Ksp} + \frac{K_5\ [H^+]^2}{\gamma_{H_2CO_3}\ Ksp\ [Ca^{2+}]}$$

$$+ \frac{K_6\ [H^+]}{\gamma_{HCO_3^-}\ Ksp\ [Ca^{2+}]} + \frac{1}{\gamma_{CO_3^{2-}}\ Ksp\ [Ca^{2+}]}$$

$$= 0.001 \qquad 4.39$$

$$T_{H^+} = \frac{-K_2\ [H_2O]\ [Ca^{2+}]}{\gamma_{CaOH^+}\ [H^+]} + \frac{K_3\ [H^+]}{\gamma_{CaHCO_3^+}\ K_{sp}} + \frac{2K_5\ [H^+]^2}{\gamma_{H_2CO_3}\ Ksp\ [Ca^{2+}]}$$

$$+ \frac{K_6\ [H^+]}{\gamma_{HCO_3^-}\ Ksp\ [Ca^{2+}]} + \frac{[H^+]}{\gamma_{H^+}} - \frac{K_9\ [H_2O]}{\gamma_{OH^-}\ [H^+]} = 0.00 \qquad 4.40$$

Note that Equations 4.38 through 4.40 now contain only $[Ca^{2+}]$ and $[H^+]$ terms as unknowns. Carbonate ion activity has been eliminated as a component and the dimensions of the Jacobian matrix to be calculated during the Newton-Raphson iteration sequence have been reduced. For more complicated systems that may contain a number of solids (Type 3, 4, 5), the process of eliminating variables is more complicated. A priority order of thermodynamic stabilities of each solid is established by comparing the appropriate ion activity products (IAP) existing during each iteration step with the corresponding solubility products. The logarithmic ratio of these terms (saturation index) is calculated in the solubility submodel and used to establish the stability order for precipitation or dissolution of solids.

$$\text{Saturation Index} = \log \left(\frac{IAP}{Ksp}\right) \qquad 4.41$$

If the saturation index for a particular mineral is negative, the system is undersaturated with respect to that mineral. If the index is positive, the solution is supersaturated and MINTEQA1 will precipitate the solid in question until the equilibrium condition is satisfied, i.e., until:

$$\log \left(\frac{IAP}{K_{sp}}\right) = 0 \qquad 4.42$$

Undersaturation for a given mineral can arise from three situations: a) a less soluble mineral phase could be controling the activities of one or more common ions, b) the component input concentrations are insufficient to exceed the solubility product, or c) free solution ion activities are limited by sorption reactions.

The MINTEQA1 program re-evaluates the saturation indices for each solid during each iteration step using the activity coefficient and log K corrections noted earlier. During the iteration sequence various solid phases may precipitate or redissolve as dictated by the saturation index. Because the formation of solid phases changes the equilibrium species distributions, the inclusion of a large number of Type 4 or 5 solids in MINTEQA1 executions requires that the species distribution equilibria problem be re-solved several times during the iteration sequence for precipitating solids. The difficulty of obtaining convergence is increased accordingly. For this reason, model systems should be spared unnecessary detail. Users should note that normally only one, or sometimes two or three solids control the free solution activities of species representing a given metal. Users working with a given system can benefit from results of pilot model runs to refine their solids lists. The initial rule is, "if in doubt leave it out." The saturation index listings can be used to detect first-pass mistakes. All unprecipitated (supersaturated) solids will be represented by a positive (>0) saturation index. If any positive values are found, the user may then add

the omitted solid and repeat the execution. It also would be prudent to eliminate any solids initially included, but which did not precipitate (i.e., sat. index <0). In the final analysis, all controlling solids (those that actually precipitate) will be identified with saturation indices equal to zero. Others need not have been included and execution time would have been reduced had they been left out.

Imposition of a fixed gas phase on the example $CaCO_3$ system would have much the same effect mathematically as adding a Type 3 calcite phase. When a carbon dioxide (CO_2) gas phase is present, the following reaction would apply.

$$CO_3^{2-} + 2H^+ \text{ <===> } CO_2(g) + H_2O \qquad 4.43$$

The corresponding mass action expression would be represented by

$$\frac{[P_{CO_2}]\ [H_2O]}{[CO_3^{2-}]\ [H^+]} = K \quad ; \log K = 18.16 \qquad 4.44$$

where $[P_{CO_2}]$ = the partial pressure of CO_2 and the other terms are the respective species activities. For systems open to the atmosphere, P_{CO_2} is fixed at about $10^{-3.5}$ atmospheres. PRODEFA1 accommodates this constraint by incorporating the fixed partial pressure term into the equilibrium constant for Equation 4.44. If PRODEFA1 is not used to assemble the input file, the user is expected to calculate the log K of the gas at the chosen partial pressure and enter it manually into the input file. In this case, log $[P_{CO_2}]$ = -3.5, the initial log K = 18.16 and the new log K' becomes

$$\log K' = 18.16 - (-3.5) = 21.66 \qquad 4.45$$

Users should note that it is possible to overconstrain a system (eliminate all degrees of freedom) by entering too many fixed species. If, for instance, a user simultaneously fixed $[P_{CO_2}]$ and the pH and entered carbonate as a component, there would be no remaining variables in Equation 4.44 and the system would be overconstrained. In this case, MINTEQA1 would eliminate carbonate as a component and remove the carbonate mass balance expression. In so doing, the carbonate ion activity is calculated from the fixed pH and dissolved CO_2 levels.

In introducing the $CaCO_3$ problem originally, the gas phase reactions were purposefully excluded. If this problem had been executed using MINTEQA1, the user would have been reminded of this exclusion in the output listing for Type 6 (excluded) species. Other Type 6 species include components that do not have corresponding mass balance equations. Examples are the electron (e^-) and the adsorption potentials used as components in defining sorption equilibria in the constant capacitance and triple-layer sorption models.

Sorption algorithms

Six options are available in MINTEQA1 for modeling sorption processes. These include: 1) the activity K_d model, 2) the activity Langmuir model, 3) the activity Freundlich model, 4) the ion exchange model, 5) the constant capacitance model, and 6) the triple-layer model. Thermodynamic data for the sorption models are not included in the MINTEQA1 database. Use of any of the sorption models, therefore, requires that users have their own data sets available. Mathematical formalisms, input data requirements, and formatting details of the individual sorption models are discussed in the separate sections below.

Activity K_d sorption model

The activity K_d sorption model is similar in some respects to the simple partition coefficient concept of sorption in which the partition coefficient is defined as the ratio of sorbate ion concentrations in the sorbed phase relative to its concentration in the equilibrium sorbate solution. That is, if we represent the sorption reaction as

$$\overline{SOH} + M \quad <===> \quad \overline{SOHM} \qquad 4.46$$

where $\overline{SOH}$ represents an unoccupied sorbent site and M is a dissolved sorbate ion, then the conventional partition coefficient (K_p) would be defined by

$$K_p = \frac{(\overline{SOHM})}{(M)} \qquad 4.47$$

Where:

$(\overline{SOHM})$ = concentration of the sorbed complex

(M) = concentration of M in the equilibrium solution

The MINTEQA1 activity K_d concept differs from this conventional representation in two important aspects. Because the unknowns in a MINTEQA1 problem are the free solution activities (as opposed to analytical concentrations) of the components, the conventional partition coefficient in Equation 4.47 must be redefined in terms of species activities. Also, because the conventional partition coefficient expression does not account for the total mass (or concentration) of unreacted sorbent sites ($\overline{SOH}$) initially available, the sorbent is presumed to exist at constant activity equal to 1.0. The mass action expression for reaction 4.46 then becomes

$$K_d^{act} = \frac{[\overline{SOHM}]}{[M]} \qquad 4.48$$

Where:

[M] = the free solution activity of the sorbate M at equilibrium

$[\overline{SOHM}]$ = the activity of the sorbed complex

By expressing the "activity K_d" in this way, the dependence of the conventional K_p on speciation distributions has been eliminated; however, users should note that charge balance constraints and electrostatic interactions are not considered in Equation 4.48. This formalism also assumes that only one species of a given component is participating in the sorption process (the free component ion, M). Only component species are allowed to enter into sorption reactions in the MINTEQA1 program. In reality, several complex species may participate, but are seldom if ever distinguished in conventional partitioning experiments. To illustrate this point, consider the calcium-containing species discussed in the $CaCO_3$ equilibria problem (Ca^{2+}, $CaOH^+$, $CaHCO_3^+$ and $CaCO_3(aq)$). In the activity K_d treatment, it is common to consider only the Type 1 components (Ca^{2+}) as sorbates even through $CaOH^+$, $CaHCO_3^+$ and $CaCO_3(aq)$ may, in this case also adsorb, but to a lesser degree. After making this assumption, the "K_d" required to operate the activity K_d algorithm is simply related to the conventional concentration-based partition coefficients most commonly available.

$$K_d^{act} = K_p \frac{(M)}{\gamma_m} \qquad 4.49$$

Where:

K_d^{act} = input constant required by MINTEQA1

K_p = conventional concentration-based partition coefficient

(M) = analytical sorbate component concentration

γ_m = activity coefficient of component M in solution

A more detailed derivation of the complexities that arise when Type 2 species sorbates are considered is given in the PRODEFA1 help text available on-line. This section may be addressed under the menu heading ACTIVITY KD. Where sorption of complex species are involved, the equilibrium constant for the component reaction to form the complex must be incorporated into the calculation of a suitable K_d.

For component-only sorption treatment using the activity K_d algorithm, users need only enter the sorption site as a component (No. 990), specify that it is a Type 3 species with activity fixed at unity, and insert the proposed reaction with an equilibrium constant equal to K_d^{act}.

Activity Langmuir Sorption Algorithm

The simple (as distinguished from the "competitive" type) Langmuir sorption isotherm can be derived from the mass action expression for the sorption reaction and the mass balance equation for the sorption site.

$$M + \overline{SOH} \overset{K_L}{<===>} \overline{SOHM} \qquad \text{(mass action)}$$

$$K_L^{act} = \frac{[\overline{SOHM}]}{[M]\,[\overline{SOH}]} \qquad 4.50$$

Where:

K_L^{act} = Langmuir constant

$[\overline{SOHM}]$ = activity of complexed sorbent sites

$[\overline{SOH}]$ = activity of unreacted sorbent sites

$[M]$ = equilibrium activity of the sorbate species

and

$$(\overline{SOH_T}) = (\overline{SOHM}) + (\overline{SOH}) \text{ (mass balance)} \qquad 4.51$$

Where:

$(\overline{SOH_T})$ = total concentration of sorbent sites available

$(\overline{SOH})$ = concentration of unreacted sorbent sites

$(\overline{SOHM})$ = concentration of complexed sorbent sites

Assuming that the activities and concentrations are equal, the combined mass balance and mass action expressions yield the Langmuir relationship.

$$(\overline{SOHM}) = \frac{K_L\,(\overline{SOH_T})\,(M)}{1 + K_L\,(M)} \qquad 4.52$$

The primary difference between the Langmuir and activity K_d treatments is that the Langmuir equation accounts for mass balance of the sorbent sites.

For this reason, the analytical concentration of sorbent sites must be input when introducing species 990 ($\overline{SOH_T}$) as a component. Otherwise, modeling details are similar and the same limitations apply. The variation in ($\overline{SOH_T}$) with system pH is not considered, for instance. Users should take care in assuring that the K_L^{act} values selected apply to systems at pH's near those being modeled. It also is important to remember that the K_L used is an "activity" K_L rather than the conventional concentration-based constant.

A meaningful way to employ commonly available "concentration" K_L data is to model the experimental supernatant solution in which the K_L was determined and replot the data in terms of the MINTEQA1 activities of the sorbate. To do this, the Langmuir isotherm is first rewritten in the linear form.

$$\frac{(M)}{(\overline{SOHM})} = \frac{1}{K_L\,(\overline{SOH_T})} + \frac{(M)}{(\overline{SOH_T})} \qquad 4.53$$

If the Langmuir isotherm accurately describes the system, a plot of $(M)/(\overline{SOHM})$ will yield a straight line of slope $1/(\overline{SOH_T})$ and intercept $1/K_L(\overline{SOH_T})$. Conventionally, the constant K_L is obtained by dividing the slope by the intercept. The K_L^{act} can be derived from an analogous plot in which the MINTEQA1 sorbate activities [M] are plotted in place of the sorbate concentration terms (M).

Activity Freundlich Algorithm

The mass action expression representing the Freundlich isotherm can be written

$$SOH + (1/n)\ M^{m+} \overset{K_f^{act}}{<====>} SOHM^{m+} \qquad 4.54$$

$$[SOHM^{m+}] = K_f^{act}\ [M^{m+}]^{1/n}$$

Where:

$[SOHM^{m+}]$ = activity of the sorbed complex

$[M^{m+}]$ = activity of the sorbate species in the equilibrium solution

$1/n$ = stoichiometric coefficient of the sorbate

This is similar to the activity K_d relationship except that the stoichiometric coefficient of the reacting species is 1/n. For the special case where n = 1, the Freundlich and activity K_d mass action expressions are identical. The K_f^{act} also is derived from conventional concentration K_f

data in an analogous way. The logarithmic (linear) form of the Freundlich mass action expression is

$$\log [SOHM^{m+}] = \log K_f + 1/n \log [M^{m+}] \qquad 4.55$$

If the Freundlich isotherm is applicable to a given system, a plot of log $[SOHM^{m+}]$ versus log $[M^{m+}]$ will yield a straight line of slope 1/n and intercept log K_f^{act}. Conventional concentration data usually involve "concentration" plots rather than activities. The K_f values from these plots can be converted to K_f^{act}'s by using MINTEQA1 to speciate the equilibrium solution at each point along the isotherm and replotting the sorption isotherm in terms of log $[M^{m+}]$ rather than log (M^{m+}). The resulting intercept will be the K_f^{act} required by MINTEQA1. Alternatively, one can simply "guess" at the activity coefficient of the sorbate for each concentration along the curve.

Like the activity K_d approach, the Freundlich isotherm does not incorporate a mass balance expression for the sorbent site. MINTEQA1 sets [SOH] to unity regardless of the activity guess entered in the input file. The mass balance stoichiometric coefficients for both the sorption sites and components are one; however, the mass action stoichiometry for the sorbate is 1/n in the Freundlich mass action expression.

Ion Exchange Sorption Algorithm

Ion exchange sorption is defined as the process by which an ion from solution is exchanged for one on the solid surface. The relative abilities of solute ion species to compete for surface sites is governed by intrinsic factors and their solution activities. Unlike the previous isotherm, the ion exchange algorithm does not assume the sorption site was bare at the outset; a native ion is expelled from the site during the sorption process and a "competitive" situation results. The mass action ion exchange relationship can be expressed as

$$M_2^+ + \overline{SOHM_1} \quad \overset{K_{ex}}{<====>} \quad M_1^+ + \overline{SOHM_2} \qquad 4.56$$

$$K_{ex} = \frac{[M_1^+]\ [\overline{SOHM_2}]}{[M_2^+]\ [\overline{SOHM_1}]}$$

where M_1^+ is the ion initially present on the exchanger and M_2^+ is the component ion to be sorbed. Both ions are present in solution and compete for the exchange sites.

MINTEQA1 uses the mathematical formalism for ion exchange that was adopted in the PHREEQE model (13). In this formalism, the activity ratio

$[\overline{SOHM_2}]/[\overline{SOHM_1}]$ is fixed. This is equivalent to assuming that the mass of sorbent $SOHM_1$ initially available is infinitely large such that $[SOHM_1]$ does not change significantly when M_1^+ ions are expelled to solution even though a substantial increase in $[M_1^+]$ results. With the ratio $[\overline{SOHM_2}]/[\overline{SOHM_1}]$ fixed, a new exchange constant K'_{ex} can be defined such that

$$K'_{ex} = K_{ex} \frac{[\overline{SOHM_1}]}{[\overline{SOHM_2}]} = \frac{[M_1^+]}{[M_2^+]} \qquad 4.57$$

Selectivity coefficients (K'_{ex}'s) can be derived from the literature for most common ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, etc., but are seldom available for trace metals. In using the ion exchange algorithm, users must supply the reaction stoichiometries and selectivity constants and specify that sites were initially saturated with the chosen native ion. Note also that reaction stoichiometries must change relative to the example given if multivalent species are sorbed.

Constant Capacitance and Triple-Layer Sorption Algorithms

All four sorption models discussed thus far neglect the electrostatic influences of charged sorbent surfaces on the nearby solution and the counter influences of changes in sorbent surface charge due to solution composition. Many colloidal sorbents carry significant surface charges that create electrostatic potentials extending into the suspending solutions. Solution ions of like charge are repelled exponentially and ions of opposite charge are attracted. Because of this, the electrostatic potentials associated with charged sorbents strongly influence the sorptive behavior of charged species. This effect results from the fact that the activities of sorbate ions approaching charged surfaces are modified by the electrical work necessary to penetrate the zone of electrostatic potentials (ψ's) extending away from the surface.

Several models are available to account for these effects in various degrees of detail. Readers are refered to Westall and Hohl's (20) excellent review for clear comparisons of the presently available surface complexation/electrostatic models. The discussion that follows will be limited to brief descriptions of the two surface complexation model options provided in MINTEQAI; the constant capacitance model and the triple layer model. These two models are closely related in many ways. Each treats the sorption process as a surface complexation reaction and accounts for the electrostatic potentials extending from the charged sorbent surface. They differ primarily in the types of surface species considered and the theoretical constructs used to develop the mathematical formalisms relating surface charge (σ) to electrostatic potentials (ψ) near surface planes and in the diffuse ion layer.

Most of the surface complexation models available were developed to describe sorption reactions in crystalline oxide systems (4). They also have been applied with reasonable success to pure amorphous iron oxyhydroxide systems (2, 5) and more recently to clay systems (11). The large body of experimental evidence that has accumulated from laboratory bench studies of pure oxide systems indicates that surface complexation models can predict adsorption behavior. Unfortunately, few data exist for applying these models to natural systems where complex mixtures of impure amorphous oxides, clays, and humic materials make up the sorbent matrix. Freshly prepared laboratory oxide systems often behave differently from the aged, impure mixtures found in the environment. The interactions are such that properties of the mixture as a whole are not necessarily those obtained by summing the properties of the individual components. Care must be used in selecting input parameters for MINTEQA1's surface complexation model algorithms in natural systems.

The constant capacitance and triple layer models both treat trace metal sorption reactions as complexation reactions analogous to the formation of complexes in solution. Surface sites are represented as SOH groups where S's are metals associated with the solid structure and located at the solid-liquid interface. Some ions, such as H^+, OH^-, and a variety of trace metal ions are presumed to be specifically adsorbed at the surface via complexation with the surface sites. With the constant capacitance model, all specifically adsorbed ions contribute to the surface charge (σ). However, in the triple layer model, only H^+ and OH^- are "potential-determining" ions. (Trace metals are presumed to reside in the 'b' plane.) Because the electrical potentials gradients extending away from the surface are the direct result of the surface charge, the specifically adsorbed potential determining ions also govern distributions of counter ions in the diffuse layer zone. Common solution ions such as Na^+, K^+, Ca^{2+}, Cl^-, SO_4^{2-} etc. are not strong complexers and are usually not strong contributors to the surface charge. Also, because trace metals are usually present at relatively low solution activities, the species H^+ and OH^- are usually the dominant contributors.

Activities of ions near the surface are influenced by the presence of electrostatic potentials arising from of the surface charge. The activity difference is the result of electrical work that must be performed in moving sorbate ions across the potential gradient between the charged surface and the bulk solution. The activity change between these zones is related to the ion charge (z) and the electrical potential (ψ) near the surface and can be expressed using the exponential Boltzmann expression,

$$[M_s^z] = [M_{aq}^z]\, e^{-zF\psi/RT} \qquad 4.58$$

Where:

$[M_s^z]$ = activity of a metal M of charge z near the surface

$[M_{aq}^z]$ = corresponding activity of M in bulk solution outside the influence of the charged surface

$e^{-zF\psi/RT}$ = Boltzmann factor

F = Faraday constant

R = ideal gas constant

T = absolute temperature

The Boltzmann factor is associated with an additional MINTEQA1 electrostatic potential input component (designated XPSIO) and appears in the mass action expressions representing surface complexation reactions as an activity coefficient correction. Since there is no analytical input of total surface charge $T(\sigma)$, these electrostatic components are unique. The total charge must be calculated from the mathematical formalisms relating surface charge to electrostatic potentials.

$$\sigma = f(\psi) \qquad 4.59$$

and

$$T(\sigma) = f(\psi) \text{ (constant)}$$

Where the constant accommodates a unit conversion from coulombs of charge per square meter to moles of charge per liter. The constant capacitance and triple layer models use different mathematical formalisms ($f(\psi)$'s) to relate σ and ψ. In both cases, the mass balance relationship used to check convergence of each electrostatic component is

$$Y(\sigma) = \sum_{i}^{n} [a(i, \sigma)\, C_i] - T(\sigma) \qquad 4.60$$

Where:

$Y(\sigma)$ = the difference function, which converges to zero as the final solution is approached

$a(i, \sigma)$ = the stoichiometric coefficients of the electrostatic component to species i

C_i = concentration of species i

n = number of species involved

Other details specific to the constant capacitance or triple layer models are discussed in separate sections below.

a) Constant Capacitance Model

In the constant capacitance model, all specifically adsorbed ions are considered potential determining species and are located in the surface ('0') plane (Figure 4.1). The double layer capacitance (C^{ℓ}) is taken to be constant and the surface charge (σ_o) and electrostatic potential are related by

$$\sigma_o = C^{\ell}\psi_o \qquad 4.61$$

Where:

ψ_o = the surface potential

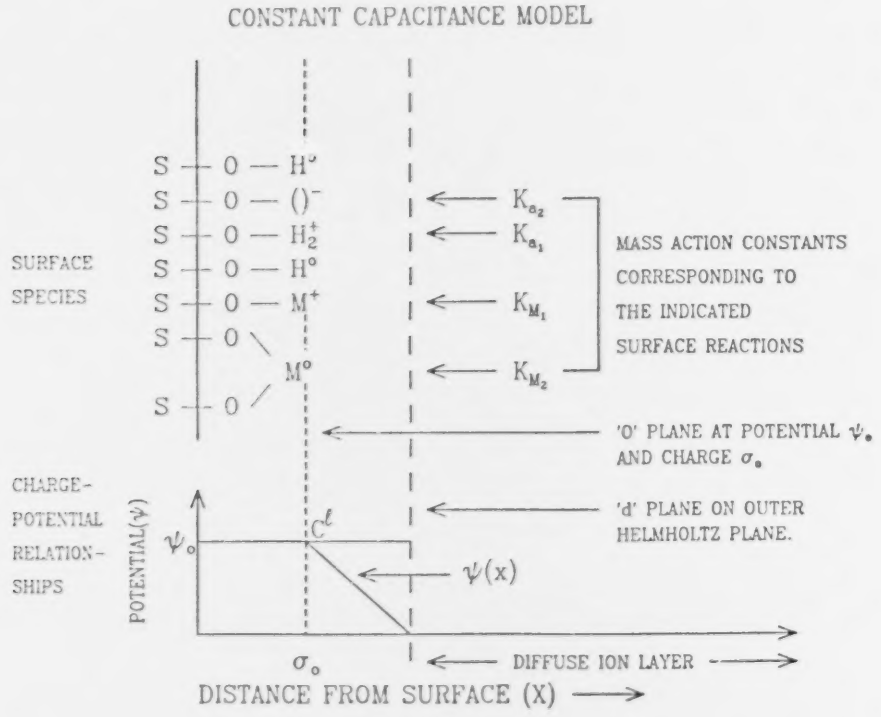

Figure 4.1. Schematic representation of the surface charge/potential relationships used in the Constant Capacitance Sorption model. Surface species indicated correspond to reactions 4.62, 4.66, 4.68 and 4.69 and mass action expressions for K_{a1}, K_{a2}, K_{M1}, and K_{M2} in Equations 4.63, 4.67, 4.70 and 4.71 as discussed in the text.

Surface sites are represented by the component SOH (ID number 990), which is treated as a conventional ligand group.

Sorption processes are written as reactions between components to form complexes and are represented by conventional mass action expressions with one key exception. The electrostatic interaction between the charged sorbate ions and the charged sorbent surface requires that electrical work be performed in moving the sorbate ion from bulk solution to the surface 'o' plane. Said differently, the activity coefficients of ions near the surface are different from those of the same ion in bulk solution due to the electrostatic potential originating at the surface. To accommodate this effect, the mass action expressions incorporate the Boltzmann factors discussed earlier as activity corrections. Ion charge and reaction stoichiometries must be used in incorporating the Boltzmann factors. A few surface complexation reactions and the corresponding mass action expressions are given below to illustrate the use of Boltzman factors. Consider the protonation reaction

$$\overline{SOH} + H_s^+ \overset{K_{a_1}}{<===>} \overline{SOH_2^+} \qquad 4.62$$

where H_s^+ denotes a hydronium ion near the surface. The corresponding mass action expression would be

$$K_{a_1} = \frac{[\overline{SOH_2^+}]}{[\overline{SOH}]\ [H_s^+]} \qquad 4.63$$

where brackets "[ ]" denote activities.

In MINTEQA1's constant capacitance model, the surface species are presumed to have activity coefficients equal to unity and the terms $[\overline{SOH_2^+}]$ and $[\overline{SOH}]$ need no further conversion; however, the activity of the surface hydronium ions must be corrected for the energy expended in moving them to the surface where the final complex formed. This is accomplished by expressing $[H_s^+]$ in terms of the bulk solution hydronium ion activity $[H^+]$ (i.e., in terms of the original Type 1 component species for which MINTEQA1 will find a solution). In this case the Boltzmann equation is written

$$[H_s^+] = [H_{aq}^+]\ e^{-F\psi_o/RT} \qquad 4.64$$

where $[H^+]$ is the bulk solution hydronium ion activity and z = 1.

The mass action expression used in MINTEQA1 is obtained by substituting this expression into Equation 4.63.

$$K_{a_1} = \frac{[\overline{SOH_2^+}]}{[\overline{SOH}]\ [H_{aq}^+]\ e^{-F\psi_o/RT}} = \frac{[\overline{SOH_2^+}]}{[SOH]\ [H_{aq}^+]}\ e^{F\psi_o/RT} \qquad 4.65$$

For the corresponding deprotonation reaction

$$\overline{SOH} \overset{K_{a_2}}{<===>} \overline{SO^-} + H_s^+ \qquad 4.66$$

the surface hydronium ion activity term $[H_s^+]$ appears as a product and the Boltzmann factor enters into the numerator of the mass balance expression.

$$K_{a_2} = \frac{[\overline{SO^-}]\ [H_s^+]}{[\overline{SOH}]} = \frac{[\overline{SO^-}]\ [H_{aq}^+]}{[\overline{SOH}]}\ e^{-F\psi_o/RT} \qquad 4.67$$

Reactions 4.62 and 4.66 involved transport of only one monovalent species (H^+) across the potential gradient. For multivalent species, both ion charge and stoichiometric coefficients must be considered. These formalisms can be illustrated for reactions of a divalent ion M^{2+}. Consider for instance the reactions

$$\overline{SOH} + M_s^{2+} \overset{K_{M_1}}{<===>} (\overline{SO^- - M^{2+}})^+ + H_s^+ \qquad 4.68$$

and

$$(\overline{SOH})_2 + M_s^{2+} \overset{K_{M_2}}{<===>} ((\overline{SO^-})_2 - M^{2+})^o + 2H_s^+ \qquad 4.69$$

In reaction 4.68 the hydronium ion is expelled to the bulk solution (Boltzmann factor in numerator) and M^{2+} is moved across the potential gradient in the other direction.

The corresponding mass action expression for reaction 4.68 is

$$K_{M_1} = \frac{[(\overline{SO^- - M^{2+}})^+]\ [H_s^+]}{[\overline{SOH}]\ [M_s^{2+}]}$$

$$= \frac{[(\overline{SO^- - M^{2+}})^+]\ [H_{aq}^+]\ e^{-F\psi_o/RT}}{[\overline{SOH}]\ [M_{aq}^{2+}]\ e^{-2F\psi_o/RT}} \qquad 4.70$$

$$= \frac{[(\overline{SO^- - M^{2+}})^+]\ [H_{aq}^+]}{[\overline{SOH}]\ [M_{aq}^{2+}]}\ e^{F\psi_o/RT}$$

where $[M_{aq}^{2+}]$ and $[M_s^{2+}]$ represent ion activities in the bulk solution and near the sorbent surface, respectively.

Reaction 4.69 will be used to illustrate the formulation where both multivalent ions (M^{2+}) and stoichiometric coefficients greater than 1 (i.e., for H_s^+) occur. The mass action expression for reaction 4.69 is written

$$K_{M_2} = \frac{[(\overline{(SO^-)_2 - M^{2+}})^o]\ [H_s^+]^2}{[(\overline{SOH})_2]\ [M_s^{2+}]}$$

$$= \frac{[(\overline{(SO^-)_2 - M^{2+}})^o]\ [H_{aq}^+]^2\ e^{-2F\psi_o/RT}}{[(\overline{SOH})_2]\ [M_{aq}^{2+}]\ e^{-2F\psi_o/RT}} \qquad 4.71$$

$$= \frac{[(\overline{(SO^-)_2 - M^{2+}})^o]\ [H_{aq}^+]^2}{[(\overline{SOH})_2]\ [M_{aq}^{2+}]}$$

Notice that the two's (2's) in the exponents of the Boltzmann factors occurred for different reasons. The two in the numerator occurred because the $[H_s^+]$ term was squared (stoichiometry). In the denominator, it occurred because M^{2+} was divalent and z = 2 in Boltzmann exponent $-2F\psi_o/RT$.

Mass action expressions for all other possible surface complexation reactions are formulated similarly. The surface site (SOH) is treated as a Type 1 MINTEQA1 component. Two MINTEQA1 surface site components SOH_1 and SOH_2, are used to provide versatility in treating problems that have more than one kind of sorbent present. The ID numbers are 990 and 991, respectively, and they may be used interchangeably or together.

The mass balance expressions for the surface site components are formulated by summing all the surface species. For the reactions discussed thus far (4.62, 4.66, 4.68 and 4.69), six surface species were involved and the mass balance expression for this system would be

$$T_{SOH} = [\overline{SOH}] + [\overline{SO^-}] + [\overline{SOH_2^+}] + [(\overline{SO^- - M^{2+}})^+] + 2[(\overline{(SO^-)_2 - M^{2+}})^o] \qquad 4.72$$

This expression can be written in terms of surface species activities rather than concentrations because of the assumption (in MINTEQA1) that surface species have unit activity coefficients. The analytical input concentration for T_{SOH} must be expressed in moles of sites per liter and is calculated from

$$T_{SOH} = \frac{N_S \; S_A \; C_S}{N_A} \qquad 4.73$$

Where:

N_S = the analytically determined surface site density (number of sites/m^2)

S_A = specific surface area of the solid (m^2/g)

C_S = concentration of solid in the suspension (g/ℓ)

N_A = Avogadros' number (6.02×10^{23})

Convergence is checked using the difference expression

$$Y(\sigma_o) = \sum \text{(all charged species in the 'o' plane)} - {}^{T}\sigma_o \qquad 4.74$$

Again, using the reactions 4.62, 4.66, 4.68, and 4.69 as an example system, the charged species in the 'o' plane include $\overline{SOH_2^+}$, $\overline{SO^-}$, and $(\overline{SO^- - M^{2+}})^+$ and the total charge is

$$\sigma_o = \sum \text{(charged species in 'o' plane)} = (\overline{SOH_2^+}) - (\overline{SO^-}) + ((\overline{SO^- - M^{2+}})^+) \qquad 4.75$$

Three "electrostatic components" are used in conjunction with the electrostatic adsorption models in MINTEQA1. They are denoted by XPSIO, XPSIB and XPSID (component ID numbers 992, 993 and 994) and represent the electrostatic potentials existing at the surface 'o' plane, the 'b' plane and the 'd' plane respectively as illustrated in Figures 4.1 and 4.2. Only the XPSIO component is used with the constant capacitance model. Unlike the regular components, the electrostatic components have no mass in solution and are excluded from mass balance calculations by entering them as Type 6 (excluded) species. An activity guess must be entered for XPSIO in the constant capacitance model. Typical values for log [XPSIO] are from -0.2 to -4.0. A reasonable initial activity guess is log [XPSIO] = -1.0. The use of components XPSIB and XPSID in conjunction with the triple layer model are discussed later under the heading "Triple Layer Model."

The constant capacitance model requires inputs for C^{ℓ}, N_S, S_A, and C_S in addition to expressions for the surface complexation reactions and associated equilibrium constants (reactions 4.62, 4.66, 4.68 and 4.69 in the examples used here). These inputs are selected as follows:

1) C^{ℓ}: This is the 'o' layer capacitance in Farads/m^2. It is calculated from

$$C^{\ell} = \frac{\sigma_o}{\psi_o} \qquad 4.76$$

where the σ_o and ψ_o values used must apply to a system at the same ionic strength and having the same electrolyte composition as that used in deriving the mass action constants. A typical value for the inner layer capacitance would be about 1.4 Farads/m^2, but the value used should be based on a knowledge of the system to be modeled.

2) N_s: This is the analytically determined surface site density of the sorbent expressed in number of sites/m^2. It is used to calculate the analytical input concentration of the sorption site component SOH (ID number 990) using the expression

$$T_{SOH} = \frac{N_s \, S_A \, C_s}{N_A} \qquad 4.77$$

T_{SOH} is entered as the analytical input concentration for component SOH.

3) S_A: This is the surface area of the sorbent in m^2/g.

4) C_s: This is the concentration of the sorbent in suspension expressed in g/ℓ.

The adsorption (surface complexation) reactions are entered along with the appropriate equilibrium constants in the input file. Reactions entered there should conform to the formats used in example reactions (4.62, 4.66, 4.68, and 4.69) developed earlier. The corresponding equilibrium constants K_{a_1}, K_{a_2}, K_{M_1}, and K_{M_2} also must be entered. These should not be confused with the intrinsic constants, commonly found in the literature. All surface reactions in MINTEQA1 must be written in terms of the neutral surface sites SOH_1 and SOH_2 (components 990 or 991). Many of the values found in the literature are intrinsic constants, which are referenced to the protonated surface site SOH_2^+ (for adsorbing anions) and to the deprotonated site SO^- (for adsorbing cations). Appropriate conversion formulae are summarized in Table 4.6.

TABLE 4.6. RELATIONSHIP BETWEEN MINTEQA1 EQUILIBRIUM CONSTANTS FOR SURFACE COMPLEXATION REACTIONS AND INTRINSIC CONSTANTS COMMONLY FOUND IN THE LITERATURE

Constant for use in MINTEQA1		Intrinsic Constants
1) $\log K_{anion}$	=	$\log K_{a_1}^{int} + \log K_{anion}^{int}$
2) $\log K_{hydrated\ anion}$	=	$\log K_{a_1}^{int} + \log K_{hydrolysis\ of\ anion} + \log K_{hydrated\ anion}^{int}$
3) $\log K_{cation}$	=	$\log K_{cation}^{int} + \log K_{a_2}^{int}$
4) $\log K_{hydrated\ cation}$	=	$\log K_{a_2}^{int} + \log K_{hydrated\ cation}^{int} + \log K_{hydrolysis\ of\ cation}$

Where:

$$K_{a_1}^{int} = \frac{[\overline{SOH_2^+}]}{\overline{[SOH]}\ [H_s^+]}$$

$$K_{a_2}^{int} = \frac{[SO^-]\ [H_s^+]}{\overline{[SOH]}}$$

b) Triple Layer Model

The triple layer model differs from the constant capacitance model in several primary ways even though the two models also have much in common. In the triple layer model, only protonation and deprotonation reactions are allowed to occur at the surface ('o' plane). Other specifically adsorbed ions are allocated to the 'b' plane (Figure 4.2) and determine the charge σ_b and potential ψ_b in that zone. Nonspecifically adsorbed ions are envisioned as residing in the outer Helmholtz layer or 'd' plane and are influenced by ψ_d potentials. Basically, one additional capacitance layer has been added to the formalisms used in the constant capacitance model. Specifically, adsorbed ions other than H^+ or OH^- determine the potentials in the new layer and background electrolytes are allowed to adsorb.

Most of the inputs for the triple layer model are similar to those for the constant capacitance model except that the potentials at the 'b' and 'd' planes are introduced by the two additional electrostatic conponents XPSIB (I.D. number 993), and XPSID (I.D. number 994), respectively. Inputs for adsorbent concentration (g/ℓ), surface area (m^2/g) and inner layer capacitance (farads/m^2) are required as in the constant capacitance model. An additional entry for the outer layer capacitance (C_2) also is required. Typical values for the outer layer capacitance are around 0.2 farads/m^2.

As in the constant capacitance model, the electrostatic components have no mass in solution and are excluded in mass balance calculations. They are entered as Type 6 excluded species. Log activity guesses for components XPSIB and XPSID in the range -0.2 to -4.0 are appropriate.

Sorption reactions in the triple-layer model are represented analogously to the constant capacitance model except that three potential planes are distinguished that correspond to the 'o' plane, the 'b' plane and the 'd' plane, respectively. The Boltzmann factor activity correction terms are specific for the potential zones across which the inner and outer zone ions must respectively move (Figure 4.2). Stoichiometric coefficients on the electrostatic terms are positive for reactants and negative for products.

For monovalent electrolytes, the total 'd' plane potential is related to the total diffuse layer charge (σ_d) by the Gouy-Chapman relationship.

$$\sigma_d = -(\varepsilon\varepsilon_o RIT)^{1/2} \sinh (F\psi_d/2RT) \qquad 4.78$$

Where:

ε = dielectric constant

ε_o = permittivity in free space (8.85×10^{-12} (coulombs)^2/joule-m

I = ionic strength

MINTEQA1 also uses Equation 4.78 as an approximation for nonsymmetric electrolytes.

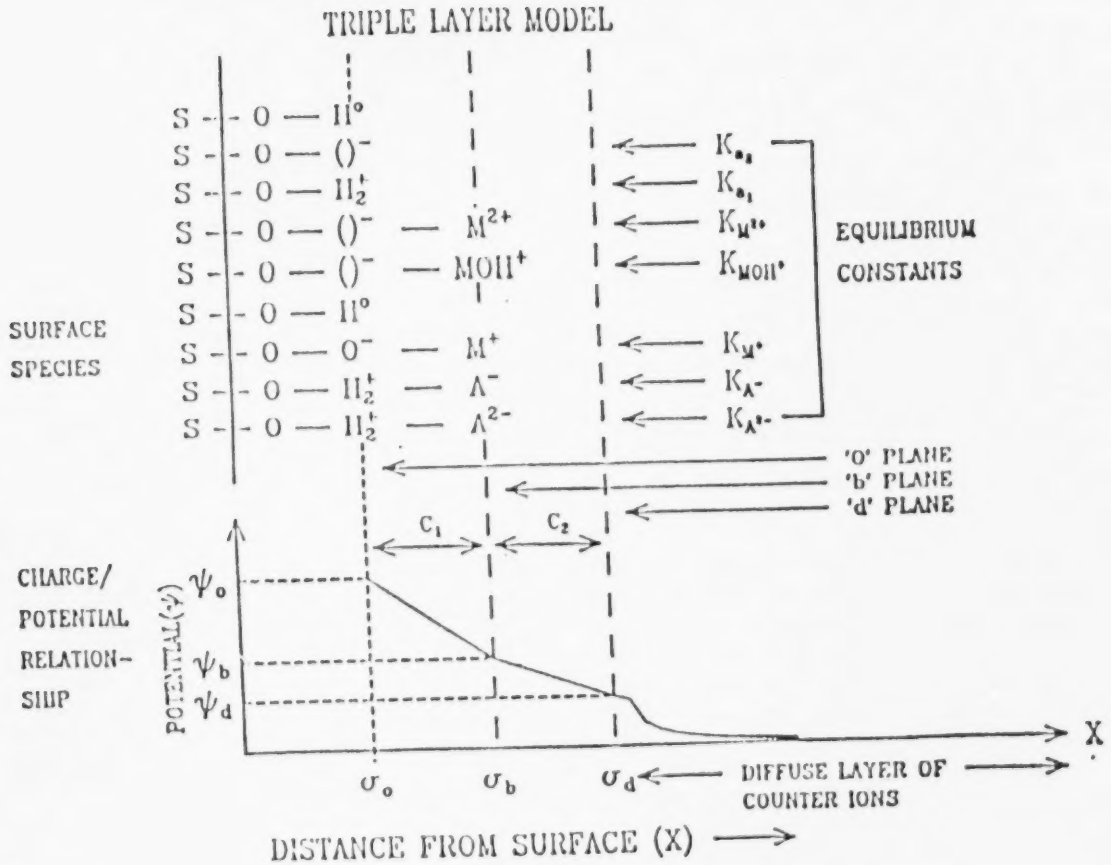

Figure 4.2. Schematic representation of surface species and charge/potential relationships in the triple layer sorption model. Nomenclature is similar to that of Figure 4.1.

Surface charges associated with the triple layer model's 'o', 'b', and 'd' planes are related to the potential differences between planes.

$$\sigma_o = C_1 (\psi_o - \psi_b)$$

$$\sigma_b = C_1 (\psi_b - \psi_o) + C_2 (\psi_b - \psi_d) \qquad 4.79$$

$$\sigma_d = C_2 (\psi_d - \psi_b)$$

Where:

σ_o, σ_b, and σ_d = surface charges associated with the 'o', 'b', and 'd' planes, respectively

C_1 and C_2 = are capacitances associated with the zones between the 'o' and 'b' planes and 'b' and 'd' planes, respectively

ψ_o, ψ_b, and ψ_d = electrostatic potentials at the 'o', 'b', and 'd' planes, respectively

Potential gradients in the inner and outer zones are linear, but potentials decay exponentially in the diffuse layer zone.

The following reactions and mass action expressions are developed to illustrate the mathematical formalisms associated with the sorption reactions depicted schematically in Figure 4.2. The mass action expressions for the reactions corresponding to equilibrium constants $^{K}a_1$ and $^{K}a_2$ in Figure 4.2 are identical to those already presented for the constant capacitance model (Equations 4.67 and 4.69) and will not be repeated here. The next reaction, representing the metal ion M^{2+} in Figure 4.2, can be written

$$\overline{SOH} + M_s^{2+} \overset{K_M 2+}{<===>} (\overline{SO^- - M^{2+}})^+ + H_s^+ \qquad 4.81$$

Where: The subscript 's' designates ions in the surface zone.

The mass action expression for $K_M 2+$ is constructed using the Boltzmann factor $e^{-zF\Delta\psi/RT}$ where $\Delta\psi$ is the potential difference through which the adsorbed or expelled ions must pass (see Equation 4.58).

$$K_M 2+ = \frac{[(\overline{SO^- - M^{2+}})^+] \; [H_{aq}^+]}{[\overline{SOH}] \; [M_{aq}^{2+}]} \; e^{\frac{-F(\psi_o - 2\psi_b)}{RT}} \qquad 4.82$$

The combined hydrolysis/sorption reaction for an M^{2+} ion (designated by K_{MOH^+} in Figure 4.2) would be expressed

$$\overline{SOH} + M_s^{2+} + H_2O \;\underset{}{\overset{K_{MOH}^{+}}{<=====>}}\; (\overline{SO^- - MOH^+})^o + 2H_s^+ \qquad 4.83$$

and the corresponding mass action expression would be written

$$K_{MOH}^{+} = \frac{[(\overline{SO^- - MOH^+})^o]\ [H_{aq}^{+}]^2}{[\overline{SOH}]\ [M_{aq}^{2+}]\ [H_2O]}\ e^{\frac{-F(\psi_o - \psi_b)}{RT}} \qquad 4.84$$

For the monovalent metal ion M^+ reaction

$$SOH + M_s^+ \;\underset{}{\overset{K_{M^+}}{<===>}}\; (\overline{SO^- - M^+})^o + H_s^+ \qquad 4.85$$

the mass action expression is

$$K_{M^+} = \frac{[(\overline{SO^- - M^+})^o]\ [H_{aq}^{+}]}{[\overline{SOH}]\ [M_{aq}^{+}]}\ e^{\frac{-F(\psi_o - \psi_b)}{RT}} \qquad 4.86$$

For the reaction of a monovalent anion (A^-) a neutral surface species results

$$SOH + A_s^- + H_s^+ \;\underset{}{\overset{K_{A^-}}{<===>}}\; (\overline{SOH_2^+ - A^-})^o \qquad 4.87$$

and the mass action expression for K_{A^-} is

$$K_{A^-} = \frac{[(\overline{SOH_2 - A^-})^o]}{[\overline{SOH}]\ [A_{aq}^{-}]\ [H_{aq}^{+}]}\ e^{\frac{F(\psi_o - \psi_b)}{RT}} \qquad 4.88$$

Note that the sign (+) on the Boltzmann factor exponent has reversed because of the negative charge on A^- and the fact that the hydronium ion term appears in the denominator.

The final reaction in Figure 4.2 for a divalent anion (A^{2-}) can be represented by

$$SOH + A_s^{2-} + H_s^+ \overset{K_{A^{2-}}}{<====>} (\overline{SOH_2^+ - A^{2-}})^- \qquad 4.89$$

The corresponding mass action expression is

$$K_{A^{2-}} = \frac{[(\overline{SOH_2^+ - A^{2-}})^-]}{[\overline{SOH}]\ [A_{aq}^{2-}]\ [H_{aq}^+]}\ e^{\frac{F(\psi_o - 2\psi_b)}{RT}} \qquad 4.90$$

The two (2) in the Boltzmann exponent arises from the divalent charge on A^{2-}.

As in the constant capacitance model, the mass balance expression for the surface site component is obtained by summing all the surface species activities. For a system involving the reactions in Figure 4.2, the mass balance expression would be

$$T_{SOH} = [\overline{SOH}] + [\overline{SOH_2^+}] + [\overline{SO^-}] + [\overline{SOH_2^+ - A^-}] + [(\overline{SO^- - M^+})^o]$$
$$+ [(\overline{SO^- - M^{2+}})^+] + [(\overline{SO^- - MOH^+})^o] + [(\overline{SOH_2^+ - A^{2-}})^-] \qquad 4.91$$

Recall that surface site species in the MINTEQA1 formulation have unit activity coefficients and the activities equal the concentrations.

Charge balance expressions for the electrostatic components representing each charged surface XPSIO, XPSIB, and XPSID can be written, respectively as

$$Y(\sigma_o) = \sum \text{(charged species in 'o')} - T(\sigma_o) \qquad 4.92$$

$$Y(\sigma_b) = \sum \text{(charged species in 'b')} - T(\sigma_b) \qquad 4.93$$

$$Y(\sigma_d) = [(-8\varepsilon\varepsilon_o RTI)^{1/2} \sinh (F\psi_d/RT) - [C_2(\psi_d - \psi_b)] \qquad 4.94$$

where we recall that

$$T(\sigma_o) = \sigma_o B \qquad 4.95$$

$$T(\sigma_b) = \sigma_b B \qquad 4.96$$

in which B is defined by

$$B = \frac{S_A \, C_S}{F} \qquad 4.97$$

Where S_A is the sorbent's specific surface area in m^2/g, C_s is the sorbent concentration in suspension in g/ℓ, and F is the Faraday constant. The summation terms in Equations 4.92 and 4.93 include all the charged species in the respective layers and may be written as follows for the system of reactions illustrated in Figure 4.2.

$$\begin{aligned} \sum (\text{charged species in 'o'}) = {} & [\overline{SOH_2^+}] + [(\overline{SOH_2^+ - A^-})^o] - [SO^-] \\ & - [(\overline{SO^- - M^+})^o] - [(\overline{SO^- - M^{2+}})^+] \\ & - [(\overline{SO^- - M^{2+}})^+] - [(\overline{SO^- - MOH^+})^o] \\ & + [(\overline{SOH_2^+ - A^{2-}})^-] \end{aligned} \qquad 4.98$$

$$\begin{aligned} \sum (\text{charged species in 'b'}) = {} & [(\overline{SO^- - M^+})^o] - [(\overline{SOH_2^+ - A^-})^o] \\ & + 2[(\overline{SO^- - M^+})^+] + [(\overline{SO^- - MOH^+})'] \\ & - 2[(\overline{SOH_2^+ - A^{2-}})^-] \end{aligned} \qquad 4.99$$

Notice that the signs (+, -) on the terms in Equations 4.98 and 4.99 relate to the charge on the part of the complex that resides in the respective zones. For instance, the overall charge on the complex species $(SOH_2^+ - A^-)^o$ in Equation 4.98 is zero, but the part of the complex that resides at the 'o' plane (SOH_2^+) has one positive charge, hence the positive (+) sign on term $[(SOH_2^+ - A^-)^o]$. The term $[(SOH_2^+ - A^-)^o]$ in Equation 4.99 has a negative (-) sign because the anionic part of the complex is located in the 'b' plane. The positive part (SOH_2^+) does not enter Equation 4.99 because it resides in the 'o' plane.

Users are cautioned that the equilibrium constants for mass action expressions presented here are <u>not</u> the intrinsic constants often reported in the literature for protonated ($\overline{SOH_2^+}$) or deprotonated (SO^-) surface sites. All MINTEQA1 reactions are based on the neutral SOH surface site. See Table 4.6 in the discussion concerning the constant capacitance model for appropriate conversion formulae.

CHAPTER 5

GETTING STARTED

The purpose of this chapter is to inform users how to use PRODEFA1 to construct input files for MINTEQA1. The quickest way of learning to assemble input files is to run through the PRODEFA1 interactive session a few times and note the changes in the resulting files as you change responses to key questions.

Users should be aggressive in trying new "branches" of the question sequence by specifying fixed solids, gas phases, redox reactions, and sorption algorithms. If some of the questions seem unclear, use the on-line help texts to get further explanations. If a question still seems unclear, just enter any answer PRODEFA1 will accept and move ahead. Some of the subsequent questions and comments may eliminate the confusion. Incorrect responses can be changed later using the editing option provided at the end of the question sequence.

A sample PRODEFA1 dialogue is provided in Appendix B to illustrate the sequence of questions involved in defining a simple $CaCO_3$ solution speciation problem. Because of its inherent simplicity, the $CaCO_3$ problem dialogue illustrates only a few of the questioning sequences represented in the program. It is provided to give readers of this manual a brief introduction to PRODEFA1.

After an input file has been assembled using PRODEFA1 and executed through MINTEQA1, the results may indicate that one or more changes need to be made in the input file. For example, the user may discover that a component was initially entered at the wrong concentration or was omitted altogether, or that the number of iterations specified was inadequate. PRODEFA1 provides the option of specifying an already existing MINTEQA1 input file for modification. During such sessions, the data from the existing file are displayed and the user is given the opportunity to change, add, or delete entries. This feature avoids time consuming duplication of effort in building MINTEQA1 input files that are substantially alike, as well as in correcting existing files. Note that when PRODEFA1 is used in this manner, the previously existing file is preserved unchanged. The modifications are specified and the modified MINTEQA1 input data are written to a new file for which the user must specify a new file name.

Structure of the MINTEQA1 Input File

A MINTEQA1 input file can consist of four basic kinds of information:

1) The problem-specific constants and options;

2) The component species;

3) The other species types that may include components or reaction products;

4) The added species that are always components or other species not present in the thermodynamic database.

All MINTEQA1 input files must have the first two kinds of information. The presence of the third and fourth kinds of data is dependent upon the specifics of the problem. In any case, it is the job of PRODEFA1 to relieve the user of actually arranging these data in the MINTEQA1 input file by engaging the user in a question-answer session from which the needed input file is produced. The four basic kinds of information listed above are discussed separately below.

INPUT FILE - Problem-Specific Constants and Options

These data are obtained by PRODEFA1 through the user's responses to straightforward questions such as:

"Enter Title--"

"Enter Temperature Between 0 and 100 Degrees C--"

There are about twelve of these questions (the exact number will depend upon the responses given by the user). Many of the questions require a yes or no ("Y" or "N") resonse. It is also possible to respond with "H" for help. PRODEFA1 will then display a brief explanation of the question and provide an opportunity to get help on related topics.

Two questions are perhaps not as straightforward as others. One of these is "Are all oversaturated solids allowed to precipitate?" If there are more than 15 to 20 components in the problem, it may be wise to answer "no" to this question. For problems that involve many components, MINTEQA1 will find many potential solids in the thermodynamic database. Most of these will not actually precipitate, but if the above question is answered yes, each will continually be checked as the problem is equilibrated. This needless complication of the problem causes longer MINTEQA1 execution times. It will usually prove much faster to run MINTEQA1 twice for such problems. The first run has a "no" response to the solids/precipitation question. At the end of the MINTEQA1 output file, all of the potential solids from MINTEQA1's database will be listed along with the final saturation index of each. In the second run, the solids/precipitation question is again answered "no", but the species ID numbers of those solids that had positive saturation indices are entered when PRODEFA1 asks for "Allowed Solids". The procedure for specifying "Allowed Solids" is explained below under the heading "INPUT FILE-Other Species Types".

The other PRODEFAl question that is not straightforward is "Do you want to run a debug case?" It is usually best to answer "no" to this question. A "yes" answer causes MINTEQAl to produce output that is only meaningful to a person familiar with the FORTRAN source code.

Some of the PRODEFAl queries are relevant only to problems that specify adsorption reactions. These are used to obtain information needed for the specific adsorption model to be used (see Chapter 4 for a description of the six available models). Examples of the information that PRODEFAl requests are adsorbent concentration, specific surface area of the adsorbent, and the electrostatic parameters for the constant capacitance and triple layer models.

The responses given by the user to questions discussed above are always used to build the first five lines of the MINTEQAl input file. The explanation below is intended to allow the user to decipher the meaning of each of these five lines when examining an existing input file. This is also useful for examining MINTEQAl output files where the input file is always reproduced.

Deciphering the First Five Lines of a MINTEQAl Input File

Line 1 - First title line

Line 2 - Second title line

Line 3 - First entry - Temperature (C°).

Second entry - Units of concentration.

Third entry - Ionic strength (0.0 means MINTEQAl is to compute ionic strength).

Line 4 - Program option flags

First entry - Inorganic carbon input option

0 = The concentration entered for the carbonate (CO_3^{2-}) component is to be treated as total inorganic carbon.

1 = The concentration entered for the carbonate (CO_3^{2-}) component is to be treated as total alkalinity.

Second entry - Debug print option

0 = Disable (this is the usual mode).

1-4 = Various arrays are output. Enter "H" for help at the debug question in PRODEFAl to learn more.

Line 4 - Program option flags (continued)

Third entry - Charge imbalance termination option

0 = MINTEQA1 execution terminates if charge imbalance exceeds 30%.

1 = Execution continues regardless of charge imbalance.

Fourth entry - Solid/precipitation output option

0 = Only those solids entered as "Allowed Solids" are considered as potential precipitates.

1 = All possible solids in the database are allowed to precipitate if their saturation indices become greater than zero. Saturation indices will be output only after the entire problem has been solved.

2 = Same as "1" except saturation indices are output after the initial solution chemistry has been solved and again after the entire problem has been solved.

3 = Same as "1" except saturation indices are output each time a solid precipitates and after the entire problem has been solved.

Fifth entry - Total number of iterations allowed

0 = 40 iterations (good first choice).

1 = 10 iterations (useful for debugging).

2 = 100 iterations.

3 = 200 iterations.

Sixth entry - Constant or variable pH option

0 - pH is to be held constant. This implies that the H^+ activity is entered as a fixed component.

1 = pH is variable. Initial H^+ activity may be specified but is not entered as a fixed component.

Line 4 - Program option flags (continued)

Seventh entry - Ionic strength option

0 = Allow MINTEQA1 to compute the ionic strength and to re-compute it at each iteration.

1 = Hold the ionic strength constant at the value specified on line 3.

Eight entry - Numerical iteration method

0 = Use the Newton-Raphson method.

1 = Use a combination of the Newton-Raphson and modified line search methods. PRODEFA1 does not ask which method the user desires. All input files created with PRODEFA1 use the Newton-Raphson method only. To use the combination method (it is sometimes helpful with problems that fail to converge), it is necessary to use a file editing or word processing program to set this entry to "1".

Ninth entry - Activity coefficient option

0 = Use Debye-Huckel equation to calculate activity coefficients.

1 = Use Davies' equation to calculate activity coefficients. Davies' equation will be used regardless of the option selected when the Debye-Huckel parameters for a species are not in the thermodynamic database.

Tenth entry - Thermodynamic data output option

0 = Do output an initial listing of data from the database.

1 = Do not output an initial listing of the thermodynamic data.

Line 5 - Adsorption parameters

First entry - Adsorption model option

0 = No adsorption.

1 = Activity K_d, Langmuir, Freundlich, or Ion Exchange models.

Line 5 - Adsorption parameters (continued)

2 = Constant Capacitance model.

3 = Triple Layer model.

Second entry - Adsorbent concentration (g/ℓ). Valid only for constant capacitance and triple layer models.

Third entry - Specific surface area of adsorbent (m^2/g). Valid only for constant capacitance and triple layer models.

Fourth entry - Inner layer capacitance (farads/m^2). Valid only for constant capacitance and triple layer models.

Fifth entry - Outer layer capacitance (farads/m^2). Valid only for triple layer model.

Sixth entry - Not used in MINTEQA1.

INPUT FILE - Component Species

As with the first kind of MINTEQA1 input file data, every input file must include a list of component species. Chapter 4 provides definitions of all species types. There are currently 72 components available in PRODEFA1 and MINTEQA1 (see Table 4.1) from which the user may specify up to 45 components (50 in the VAX version) in one MINTEQA1 run. The component species each have a unique ID number and name. PRODEFA1 will ask whether the user plans to identify the desired components by entering the ID numbers. If the user doesn't know the ID number of a desired component, PRODEFA1 will ask for the first letter in the component name and will display all components whose name begins with that letter. This feature relieves the user of memorizing component ID numbers. If the user is unable to identify the needed component among those displayed, PRODEFA1 assumes this is because that component is not in the database. PRODEFA1 then enters a series of questions that allow the user to define a new component. (The new component will be an "added species". The procedure for defining an added species is discussed below under the heading "INPUT FILE - Added Species".)

After a component is selected, PRODEFA1 queries the user for the concentration (in units specified earlier). After all desired components are entered, PRODEFA1 asks for the pH and Eh if the H^+ ion and the electron (e^-) components are not among those already specified. Also, depending on user responses that follow, PRODEFA1 may add other components. For example, the user may enter Fe^{3+} as a component but not Fe^{2+}. If the redox couple Fe^{3+}/Fe^{2+} is subsequently entered when PRODEFA1 asks for fixed-ratio redox reactions, Fe^{2+} will be added to the component list at a negligible concentration. PRODEFA1 will notify the user that Fe^{2+} has been added. Selection of

certain adsorption models also triggers automatic additions to the component list.

PRODEFAI sets the initial activity guess of each component to be equal to the concentration. The value that PRODEFAI enters in the MINTEQAI input file is the common logarithm of the activity guess. If a solid, fixed or finite, is specified as initially present (an explanation of how to do this can be found under the heading "INPUT FILE - Other Species Types"), PRODEFAI will examine the user's input concentrations for those aqueous components that comprise the solid and will adjust the concentrations up or down so as to conform to the solubility product for the solid. For this reason, the concentrations of those components in the MINTEQAI input file may differ from the concentrations initially specified by the user.

INPUT FILE - Other Species Types

Other species types include fixed species (those whose activities are required to be invariant), finite solid species, allowed (potential) solid species, and excluded species (those species that are to be excluded from mass balance calculations in MINTEQAI). The fixed and excluded species may include species that are also components. For example, H^+ is always a component species but may also be a fixed species if the pH is to be held constant. Some of the adsorption models trigger simultaneous additions to the component species and the excluded species.

Fixed species can be components, redox couples, or gas or solid phases (fixed solid phases are sometimes referred to as "infinite solids" to distinguish them from finite solids). For fixed component species, PRODEFAI enters the negative log of the activity along with the species ID and name in the MINTEQAI input file. For gas or solid phases, or redox couples, PRODEFAI enters the log of the equilibrium constant and the standard enthalpy change (after giving the user an opportunity to modify them) along with the ID number and name. These values are obtained by PRODEFAI from the thermodynamic database after the user has identified the species by giving its ID number. If the ID number is unknown and the species desired is a gas or redox couple, PRODEFAI displays a list of all gases and redox reactions in the database. The user then selects the desired entry. If the desired species is a solid, PRODEFAI displays the list of major mineral groups shown in Table 5.1. The user selects the group to which the desired solid belongs by entering the two-digit code associated with the group. PRODEFAI responds by asking for the first letter in the name of the component that serves as the major cation. When the component has been identified, PRODEFAI searches the thermodynamic database for all solids that meet the two identifying criteria. These are displayed and the user selects the appropriate solid.

As was noted for component species, if the user is attempting to define a fixed species and is unable to identify it among the possibilities displayed on the screen, PRODEFAI assumes this is because that species is not in the database and a series of questions follow that allow the user to define a new species. Upon successfully defining the new species, PRODEFAI enters it in the MINTEQAI input file as both a fixed species and an "added species".

TABLE 5.1. MINERAL GROUP ID CODES USED IN FORMING SOLIDS ID NUMBERS

Mineral Group ID Numbers			
00	elements	60	sulfates
10	sulfides	61	selenites, selenates
20	oxides and hydroxides	70	phosphates
30	multiple oxides	71	arsenates
40	bromides	73	vanadates
41	chlorides	74	molybdates, molybdites
42	fluorides	75	uranates
43	iodides	76	tungstates
50	carbonates	80	orthosilicates
51	nitrates	82	chain silicates
52	borates	84	framework silicates
53	chlorates	86	sheet silicates

PRODEFAl enters all fixed species, whether they are also added species or not, as Type 3 in the MINTEQAl input file.

Finite solid species differ from infinite (fixed) solids in that their activities are not held constant while the problem is equilibrated. They may dissolve partially or completely. Thus, for finite solids, MINTEQAl must know the mass initially present. PRODEFAl obtains this value from the user and in all other respects, the procedure for defining finite solids is identical to that for infinite solids. Finite solids are entered as Type 4 in the MINTEQAl input file.

As noted in the discussion concerning component species, PRODEFAl adjusts the concentrations of those components that comprise solids that are initially present so as to conform to the solubility product of the solid.

Allowed or potential solids are those that are not initially present but are to be allowed to precipitate if their solubility product is exceeded. They differ from finite solids only in that their initial mass is zero. They are identified to PRODEFAl exactly as are the fixed and finite solids. Once identified, PRODEFAl will display the log of the equilibrium constant and the standard enthalpy change for the user to modify if desired. PRODEFAl enters the allowed solids as Type 5 in the MINTEQAl input file. When, during MINTEQAl's iterations, an allowed solid precipitates, MINTEQAl re-assigns it to Type 4, finite solid.

Species that might be excluded for a specific problem include one or more of that problem's components or any species present in the thermodynamic

database for which the necessary reactants are among the problem's components. Excluded (or "omitted") means not included in mass balance calculations. The excluded species designation is particularly useful for those components that are actually not chemical entities such as the electrostatic components of the constant capacitance and triple layer adsorption models. PRODEFA1 includes these as excluded species without user intervention when those models are used. For other species that the user may wish to designate as excluded (Type 6 in the MINTEQA1 input file), it is only necessary to identify the species to PRODEFA1.

INPUT FILE - Added Species

Added species are always either components or other species that are not present in the thermodynamic database but are needed in the problem. The "other" species include aqueous complexes, gas or solid phases, redox couples, and adsorption products. The one restriction that applies to all added species is that the species to be added must be derivable from the components (reactants) supplied in the problem (although one or more of the components may themselves be added species). Neither components nor reactions that are added in an input file are premanently added to the database. They exist only for the problem for which they are added. Upon reading the input file, MINTEQA1 treats the type 2 species as an addendum to the thermodynamic database.

As noted earlier, PRODEFA1 attempts to aid the user in identifying desired components and other species. When these attempts fail, PRODEFA1 assumes that the desired component or other species is not in the database and asks whether the user wishes to define a new species. On a "yes" response, PRODEFA1 proceeds through a series of questions that allow the user to designate an ID number, name, and the necessary thermodynamic data pertinent to the type of species being defined. The added species will be of the same type as that which the user was attempting to identify when the "failure to identify" occurred. For example, if the user is attempting to specify a fixed-ratio redox couple and is unable to identify it to PRODEFA1, the series of questions for defining a new species will be those pertinent for a redox couple. After the redox reaction is defined with legitimate components (it may be necessary to define one or more new components as well), the ID number and other information pertinent to the definition of the new redox couple is entered by PRODEFA1 as Type 3 along with any other fixed species in the MINTEQA1 input file.

Because there are no adsorption reactions in the thermodynamic database, PRODEFA1 always enters the question series for adding new species when an adsorption model is used.

For added species that are defined by reactions (as opposed to component species that are reactants), the user will be asked for the components that comprise the reaction along with the stoichiometry of each. The reader is referred to Chapter 4 for a description of how components are treated as reactants and how their stoichiometry is used in MINTEQA1. The explanation

that follows will serve to illustrate the stoichiometry of a familiar reaction. This reaction is already defined in the thermodynamic database and need not be defined as an added species in a MINTEQA1 input file.

$$H_2O \quad <====> \quad H^+ + OH^-$$

Should we wish to write this reaction in a way that MINTEQA1 can use, we first note that H_2O and H^+ are already components in the database. Rearranging so that components are on one side and products are on the other gives

$$H_2O - H^+ \quad <====> \quad OH^-$$

Thus, the stoichiometry for H^+ in this reaction is (-1) and for H_2O is +1. As with other features of PRODEFA1, experimentation is probably the best teacher for learning to properly define added species.

Sample Problems

Input files for four very simple $CaCO_3$ systems will be discussed here to illustrate the inputs required for modeling the systems similar to those discussed in Chapter 4.

1) System A: 0.001 molar $CaCO_3$ solution, fixed pH = 9.0, no solid or gas phases imposed, tempertaure = 20°C.

A copy of the corresponding interactive dialogue is reproduced in Appendix B. The resulting input file is shown below.

```
EXAMPLE PRODEF RUN                          -Title
CACO3 SOLUTION                              -Title
20.00 MOL      0.00                         -Temperature, units, ionic strength
0 0 1 0 0 0 0 0 1 0                         -Program option flags
0    0.00    0.00    0.00    0.00           -Adsorption option, parameters
   140  1.000E-03  -3.00                    -CO3 2- component
   150  1.000E-03  -3.00                    -Ca 2+ component
   330  0.000E+00  -9.00                    -H+ component

  3   1                                     -Begin type 3 list of 1 entry
   330  9.000E+00   0.00                    -H+1 component (fixed)
```

Explanatory comments are along the right side preceded by a dash. The first two lines are title lines. Line 3 specifies the temperature (20°C), concentration units and an indication, in the third field (0.00), that the solution ionic strength was not "fixed." Line 4 specifies user selected execution options. The first two zeros in Line 4 indicate that inorganic carbon was entered as carbonate rather

than total alkalinity and that the "debug print option" was not requested. The one (1) in the third position indicates a charge balance override is requested. The next five zeroes indicate, respectively, that 1) only Type 5 solids (of which there are none) should be considered for precipitation, 2) the total number of iterations is to be restricted to 40, 3) the pH is to be fixed (at a value entered later), 4) the ionic strength is not "fixed," and 5) only the Newton-Raphson iteration method was to be used. The ninth digit, a one(1), indicates the activity coefficients are to be calculated with the Debye-Huckel equation if the necessary parameters are available in the database, and the zero in the tenth position means that a printout of thermodynamic data was requested as a part of the output.

The first zero in Line 5 indicates no sorption algorithms were to be considered. The remaining columns for sorption parameter inputs are therefore filled with blank entries (0.00).

The first two entries beginning with Line 6 are for the CO_3^{2-} and Ca^{2+} input components which have ID numbers 140 and 150, respectively. Each was entered at an analytical input concentration of 0.001 mol/liter in the second column. The third column containing log activity guesses for each component were entered by PRODEFA1. The third component H^+ (ID = 330) was necessary because all aqueous systems have access to a source of hydronium ions resulting from dissociation of the solvent. Note that no finite analytical input mass was necessary in this case; however, a log activity guess of -9.0 was entered because the pH is to be fixed at pH = 9.0.

Following a blank line, the next has a "3" and a "1" indicating that one Type 3 species was entered. The next line contains the ID number for H^+ (330) followed by a value of 9.00 indicating that the negative log of the H^+ activity has been fixed (invariant) at a level corresponding to pH = 9.0. It is important to note that the second and third columns have different uses depending on the type of species entered. If a reaction species ID number, such as a redox couple, had been entered in place of 330, the next two columns would have been used to enter new log K values and enthalpies of reaction, respectively. Also, compare these entries with those in the fixed gas phase $CaCO_3$ problem (System C). In the latter case, the second column is used for entering the modified equilibrium constant calculated by PRODEFA1 according to the method described in Chapter 4.

2) System B: 0.001 molar $CaCO_3$ solution, floating pH, no solid or gas phases imposed, temperature = 20°C.

The input file for this problem is given below:

```
EXAMPLE INPUT FILE                          -Title
CACO3 PROBLEM FLOATING PH                   -Title
20.00 MOL    0.00                           -Temperature, units, ionic strength
0 0 1 0 0 0 0 0 0 0                         -Program option flags
0   0.00   0.00   0.00    0.00 0           -Adsorption option, parameters
```

```
140 0.100E-02  -3.00          -CO3 2- component
150 0.100E-02  -3.00          -Ca 2+ component
330 0.101E-02  -2.99          -H+ component
```

Explanatory comments are along the right side preceded by a dash. In this case, no fixed components were imposed. The input concentration for the hydronium ion component (330) was derived from a fixed pH pilot run in which the H^+ input was entered as zero. The H^+ difference (i.e., the amount of H^+ ion either generated or consumed during the reaction) was printed in the column corresponding to the equilibrium H^+ ion activity in the MINTEQA1 output.

3) System C: 0.001 molar $CaCO_3$ solution, fixed pH = 8.01, fixed CO_2 phase imposed where $^PCO_2 = 10^{-3.5}$ atm, no solid phases present, temperature = 20°C.

The input file for this system is:

```
EXAMPLE INPUT FILE                    -Title
CACO3 PROBLEM WITH CO2 GAS PHASE      -Title
20.00 MOL     0.00                    -Temperature, units, ionic strength
0 0 1 0 0 0 0 0 0 0 0                 -Program option flags
0   0.00   0.00   0.00   0.00 0       -Adsorption option, parameters
    140  1.100E-03  -3.00            -CO3 2- component
    150  1.000E-03  -3.00            -Ca 2+ component
    330  9.770E-09  -8.01            -H+ component
      2  5.550E+01   1.00
  3   2                               -Begin type 3 list of 2 entries
3301403  2.170E+01  -0.53            -CO2 (g) fixed gas
    330  8.010E+00   0.00            -H+ component (fixed)
```

Note that an analytical value for component 002 (H_2O) is entered. Also note that two fixed species are entered. The first, 3301403, corresponds to the fixed CO_2 gas phase imposed.

$$CO_2(g) + 2H_2O \;\langle==\rangle\; H_2CO_3 \qquad 5.1$$

Using the MINEQA1 components (reactants) the corresponding reaction is

$$CO_3^{2-} + 2H^+ - H_2O \;\langle==\rangle\; CO_2(g) \qquad 5.2$$

and

$$K = \frac{[^PCO_2]\ [H_2O]}{[CO_3^{2-}]\ [H^+]^2} = 10^{18.16} \qquad 5.3$$

but

$$[^PCO_2]\ [H_2O] = [^PCO_2] \qquad 5.4$$

because the activity of water = 1.0

Assuming a fixed CO_2 partial pressure of $10^{-3.5}$ atm (the usual atmospheric value). A new equilibrium constant K' can then be defined as follows to account for the fixed CO_2 pressure

$$\log K' = \log K - (\log 10^{-3.5})$$

$$= 18.16 + 3.5 \qquad 5.5$$

$$\equiv 21.7$$

This modified equilibrium constant (log K') is entered to the right of ID number 3301403 in Section 3 to accommodate the fixed gas phase. Other CO_2 partial pressures would be handled similarly. In all cases the value of log K' entered in the second column would be 18.16 minus the log of the CO_2 partial pressure in atmospheres.

The other fixed species is the hydronium ion component (330), which is fixed at an activity corresponding to pH = 8.01.

4) System D: 0.001 molar $CaCO_3$ solution, pH fixed at 8.01, calcite solid phase imposed, no CO_2 gas phase, temperature = 20°C.

The input file for this system as developed using PRODEFAI is shown below.

```
EXAMPLE INPUT FILE                          -Title
CACO3 PROBLEM WITH SOLID PHASE (CALCITE)    -Title
20.00 MOL     0.00                          -Temperature, units, ionic
                                               strength
0 0 1 0 0  0 0 0 0 0                        -Program option flags
0   0.00  0.00      0.00   0.00 0           -Adsorption option, parameters
    140 0.579E-04     0.91                  -CO3 2- component
    150 0.579E-04     0.91                  -Ca 2+ component
    330 0.977E-08    -8.01                  -H+ component

  3   2                                     -Begin type 3 list of 2 entries
5015001 0.848E+01     2.59                  -Calcite (fixed solid)
    330 0.801E+01     0.00                  -H+ component (fixed)
```

Note that the analytical inputs for both carbonate (140) and calcium ion (150) are not 0.001 molar. The values entered in response to PRODEFAI questions were 0.001 molar. PRODEFAI made these adjustments in response to the presence of a calcite phase. When the calcite phase was imposed, the concentrations of Ca^{2+} and CO_3^{2-} were adjusted to conform to the solubility product of calcite.

$$Ca^{2} + CO_3^{2-} \quad <==> \quad CaCO_3(s) \log K = 8.48 \qquad 5.6$$

The entry in column 3, line 2 corresponds to the enthalpy of reaction for reaction 5.6. The analytical concentrations for Ca^{2+} and CO_3^{2-} were calculated from the solubility products for calcite (Equation 5.6)

$$[Ca^{2+}]\ [CO_3^{2-}] = 10^{-8.48} \qquad 5.7$$

where:

$$[Ca^{2+}] = [CO_3^{2-}] = (10^{-8.48})^{1/2}$$

$$= 5.79 \times 10^{-5} \text{ molar}$$

Line 3 of Section 3 indicates the hydronium ion activity was fixed at a level corresponding to pH 8.01 as before.

The input files for a few more complicated systems are included in the on-line PRODEFAl text entries to illustrate common error responses. These examples are accompanied by brief discussions of techniques used to isolate and correct the error offenses.

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APPENDIX A

NEWTON-RAPHSON NUMERICAL METHOD

The Newton-Raphson numeric method is an iterative technique for finding a value x such that $y(x) = 0$. When only one variable is involved, successive (improved) values of x (x_n, x_{n+1}, x_{n+2} ----) are obtained from the difference quotient.

$$\frac{y(x_{n+1}) - y(x_n)}{x_{n+1} - x_n} = \left.\frac{dy}{dx}\right|_{x_n} = z_n \qquad \text{A1}$$

Where the derivative evaluated at x_n is denoted by z_n.

In each successive step, the function $y(x_{n+1})$ is set to zero (because this is the solution sought) and Equation A1 is solved for x_{n+1} in terms of the previously known values of x_n, $y(x_n)$ and z_n. When $y(x_{n+1})$ in Equation A1 is set to zero

$$z_n \, \Delta x = y(x_n) \qquad \text{A2}$$

Where $\Delta x = x_{n+1} - x_n$.

The new value of x is then found from:

$$x_{n+1} = x_n - \Delta x \qquad \text{A3}$$

Similar reasoning applies to problems in more than one variable except that the analog to Equation A2 becomes the matrix equation

$$Z_n \, \Delta X = Y_n \qquad \text{A4}$$

Where Z_n is the Jacobian of Y with respect to X evaluated at X_n. A solution for ΔX is found from Gaussian elimination and back substitution and X_{n+1} is calculated from:

$$X_{n+1} = X_n - \Delta X \qquad \text{A5}$$

APPENDIX B

SAMPLE PRODEFAI DIALOGUE FOR THE CACO3 PROBLEM

```
 Enter Name of NEW File To Be Defined (Up To 16 Characters > TESTIN.DAT

 Enter The Number Of Problems To Be Generated In  This Problem File > 1

 Will The NEW File Be A Modification Of An Old File? (Y,N,H) > N

 Enter Title (1 Of 2 Lines) > EXAMPLE PRODEF RUN

 Enter Title (2 Of 2 Lines) > CACO3 SOLUTION

 Select Data Units: 1= Molal, 2= Mg/l, 3= ppm, 4= meq/l > 1

 Enter Temperature Between 0 And 100 Degrees C > 20.0

 Fix Ionic Strength? (Y,N,H) > N

 Enter Iteration Option: 0= 40, 1= 10, 2= 100, 3= 200  > 0

 Terminate If Initial Charge Balance Off > 30% ? (Y,N,H) > N

***CAUTION: Be Aware That Answering "Y" On The Next Question And Subsequently
            Adding Certain Fixed Minerals Could Cause A Phase Rule Violation.

 Are All OverSaturated Solids Allowed To Precipitate? (Y,N,H) > N

 Want To Run A Debug Case (Additional Output)? (Y,N,H) > N

 Enter Chosen Activity Coefficient Algorithm:
                0= Extended Debye-Huckel; 1= Davies > 1

 Print Full Derived Species Data Base? (Y,N,H) > Y

 Want To Enter Species By Identifying Number? (Y,N,H) > N

** This Section Defines The Makeup Of COMPONENT SPECIES **

 ANY       AQUEOUS ELEMENTS     ? (Y,N,H) > Y

REMEMBER: Zero Concentration Fixes A Component Invariant
```

```
Enter 1st Letter Of Chem. Symbol Of Wanted AQUEOUS COMPONENT (*Ends Search)>C
  1 CO3-2          2 CA+2           3 CD+2           4 CL-1           5 CR+2
  6 CR(OH)2        7 CRO4-2         8 CS+1           9 CU+1          10 CU+2


Enter Integer For Wanted   AQUEOUS COMPONENT (0= NONE) > 1

Enter Concentration Of CO3-2                ID #       140 In   MOL   > .001
   140 CO3-2                Has Been Modified Or Added To File 1

Enter 1st Letter Of Chem. Symbol Of Wanted AQUEOUS COMPONENT (*Ends Search)>C
  1 CO3-2          2 CA+2           3 CD+2           4 CL-1           5 CR+2
  6 CR(OH)2        7 CRO4-2         8 CS+1           9 CU+1          10 CU+2


Enter Integer For Wanted   AQUEOUS COMPONENT (0= NONE) > 2

Enter Concentration Of CA+2                 ID #       150 In   MOL   > .001
   150 CA+2                 Has Been Modified Or Added To File 1

Enter 1st Letter Of Chem. Symbol Of Wanted AQUEOUS COMPONENT (*Ends Search)>H
  1 H2O            2 H3ASO3         3 H3ASO4         4 H3BO3          5 HUMATE
  6 H+1            7 HG2+2          8 HG(OH)2        9 HS-1          10 HSE-1
 11 HSEO3-1       12 H4SIO4

Enter Integer For Wanted   AQUEOUS COMPONENT (0= NONE) > 6

Enter Concentration Of H+1                  ID #       330 In   MOL   > 0.0

Enter Fixed Positive Activity Of  H+1                  In Moles/KG H2O >.1E-08

   330 H+1                  Has Been Modified Or Added To File 1

Enter 1st Letter Of Chem. Symbol Of Wanted AQUEOUS COMPONENT (*Ends Search)>*

Enter P For pE, E For Eh, N For Neither, H For Help> N

** This Section Defines The Makeup Of GASEOUS SPECIES   **

ANY      FIXED GASES          ? (Y,N,H) > N

** This Section Defines The Makeup Of ADSORPTION PROBLEM**

ANY      ADSORPTION DEFINIT°N? (Y,N,H) > N

** This Section Defines The Makeup Of REDOX SPECIES     **

ANY      FIXED-RATIO REDOX    ? (Y,N,H) > N

** This Section Defines The Makeup Of MINERAL SPECIES   **

ANY      INFINITE SOLIDS      ? (Y,N,H) > N
```

```
** This Section Defines Solids Initially Present**

 ANY       FINITE SOLIDS       ? (Y,N,H) > N

** This Section Defines Specific Solids That Could Form**

 ANY       ALLOWED SOLIDS      ? (Y,N,H) > N

** This Section Defines Species That Will Be Excluded From The Calculations **

 ANY       EXCLUDED SPECIES    ? (Y,N,H) > N

 Any Other Database Modifications Or Additions? (Y,N,H) > N


Listing Of COMPONENT        Follows For Verification Or Change
      I. D. TOTAL CONC°N LOG10(ACT)
  1      140 1.00000E-03-3.00000E+00 CO3-2
  2      150 1.00000E-03-3.00000E+00 CA+2
  3      330 0.00000E+00-9.00000E+00 H+1

 Enter Line # To Change, Add Or Delete (0= Done) > 0
No AQUEOUS SPECIES  (TYPE 2) Have Been Defined.


Listing Of FIXED SPECIES    Follows For Verification Or Change
      I. D. LOG10(KEQ)   DELTA H REAC
  1      330 9.00000E+00 0.00000E+00 H+1

 Enter Line # To Change, Add Or Delete (0= Done) > 0
No FINITE SOLID     (TYPE 4) Have Been Defined.
No POTENTIAL SOLIDS (TYPE 5) Have Been Defined.
No OMITTED SPECIES  (TYPE 6) Have Been Defined.
No ADDED SPECIES    (TYPE 7) Have Been Defined.

Any Other Detailed Changes In Definition Of Problem ?  (Y,N) > N
A Problem File Named TESTIN.DAT   Has Now Been Generated.
It Can Be Modified By This Same Program By Recalling It As The Old File.


EXAMPLE PRODEF RUN
 CACO3 SOLUTION
 T =  20.00 MOL      0.00
 0 0 1 0 0 0 0 0 1 0
 0    0.00    0.00    0.00    0.00
      140  1.000E-03  -3.00
      150  1.000E-03  -3.00
      330  0.000E+00  -9.00
 H2O HAS BEEN INSERTED AS A COMPONENT
   3    1
      330  9.000E+00    0.00
```

APPENDIX C

THE THERMODYNAMIC DATABASE USED BY MINTEQA1

Some important constants from the thermodynamic database used by MINTEQA1 are presented in the following tables along with the species ID numbers. This is not a listing of the database itself. The actual database has the stoichiometry of the components involved in each reaction as well as other constants. The table is subdivided into five parts:

1) Component Species

2) Aqueous Complexes

3) Solid Species

4) Redox couples

5) Gas phases

Concerning the notation used in naming the species, because FORTRAN does not support the use of super- or subscripts, the customary method of writing chemical formulas cannot be accommodated without modification. The following naming rules are used in MINTEQA1:

1) Stoichiometric coefficients are written with parentheses and brackets enclosing the elements in the formula to which the stoichiometry applies. The stoichiometric coefficient itself will never be preceded with a sign (+/-).

2) Species charge numbers will always be preceded with a sign (+/-). The one (1) in (+1) and (-1) may be omitted. If a species name ends with an unsigned number, that number represents stoichiometry, not oxidation
state.

3) Species names involving organics may be shortened by leaving out letters.

Examples:

H2O	means	H_2O
CR(OH)2+	means	$Cr(OH)_2^+$
HG(OH)2	means	$Hg(OH)_2^{2-}$
SO4-2	means	SO_4^{2-}
TARTRAT	means	Tartrate

Species ID Number	Name	Species Charge	Gram Formula Weight
	********** Component Species **********		
001	E-1	-1.0	0.0000
002	H2O	0.0	18.0153
020	AG+1	1.0	107.868
030	AL+3	3.0	26.9815
060	H3ASO3	0.0	125.9437
061	H3ASO4	0.0	141.9431
090	H3BO3	0.0	61.8331
100	BA+2	2.0	137.3400
130	BR-1	-1.0	79.9040
140	CO3-2	-2.0	60.0094
141	FULVATE	-2.0	650.0000
142	HUMATE	-2.0	2000.0000
143	ACETATE	-1.0	59.05
144	TARTRAT	-2.0	148.09
145	GLYCINE	-1.0	74.07
146	SALICYL	-2.0	136.12
147	GLUTAMA	-2.0	145.13
148	PHTHALA	-2.0	164.13
150	CA+2	2.0	40.0800
160	CD+2	2.0	112.3994
180	CL-1	-1.0	35.4530
210	CR+2	2.0	51.996
211	CR(OH)2+	1.0	86.011
212	CRO4-2	-2.0	115.994
220	CS+1	1.0	132.905
230	CU+1	1.0	63.5460
231	CU+2	2.0	63.5460
270	F-1	-1.0	18.9984
280	FE+2	2.0	55.8470
281	FE+3	3.0	55.8470
330	H+1	1.0	1.0080
360	HG2+2	2.0	401.18
361	HG(OH)2	0.0	234.61
380	I-1	-1.0	126.9044
410	K+1	1.0	39.1020
440	LI+1	1.0	6.9390
460	MG+2	2.0	24.3120
470	MN+2	2.0	54.9380
471	MN+3	3.0	54.9380
490	NH4+1	1.0	18.0386
491	NO2-1	-1.0	46.0055
492	NO3-1	-1.0	62.0049

Species ID Number	Name	Species Charge	Gram Formula Weight
	********** Component Species **********		
500	NA+1	1.0	22.9898
540	NI+2	2.0	58.7100
580	PO4-3	-3.0	94.9714
600	PB+2	2.0	207.1899
680	RB+1	1.0	85.4699
730	HS-1	-1.0	33.0720
731	S	0.0	32.0640
732	SO4-2	-2.0	96.0616
760	HSE-1	-1.0	79.97
761	HSEO3-1	-1.0	127.97
762	SEO4-2	-2.0	142.96
770	H4SIO4	0.0	96.1155
800	SR+2	2.0	87.6200
870	TL+1	1.0	204.37
871	TL(OH)3	0.0	255.39
891	U+4	4.0	238.0290
890	U+3	3.0	238.0290
892	UO2+1	1.0	270.0278
893	UO2+2	2.0	270.0278
900	V+2	2.0	50.94
901	V+3	3.0	50.94
902	VO+2	2.0	66.939
903	VO2+1	1.0	82.939
950	ZN+2	2.0	65.3699
990	SOH1	0.0	0.0
991	SOH2	0.0	0.0
992	XPSIO	0.0	0.0
993	XPSIB	0.0	0.0
994	XPSID	0.0	0.0
995	SOHB	0.0	0.0

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Aqueous Complexes	**********	
3300020	K OH-	13.3450	-13.9980	17.0074
3307700	KH3SIO4 -	8.9350	-9.9300	95.1070
3307701	KH2SIO4 -2	29.7140	-21.6190	94.0990
7702700	KSIF6 -2	-16.2600	30.1800	142.0760
3300900	KH2BO3 -1	3.2240	-9.2400	60.8250
902700	KBF(OH)3 -	1.8500	-0.3990	80.8310
902701	KBF2(OH)2 -	1.6350	7.6300	82.8220
902702	KBF3OH -	-1.5800	13.6670	84.8130
902703	KBF4 -	-1.7950	20.2740	86.8040
3304900	KNH3 AQ	12.4800	-9.2520	17.0300
4907320	KNH4SO4 -	0.0000	1.1100	114.1000
4603300	KMGOH +	15.9350	-11.7900	41.3190
4602700	KMGF +	4.6740	1.8200	43.3100
4601400	KMGCO3 AQ	2.0220	2.9800	84.3210
4601401	KMGHCO3 +	-2.4300	11.4000	85.3290
4607320	KMGSO4 AQ	1.3990	2.2500	120.3730
4605800	KMGPO4 -	3.1000	6.5890	119.2830
4605801	KMGH2PO4 +	-1.1200	21.0660	121.2990
4605802	KMGHPO4 AQ	-0.2300	15.2200	120.2910
1503300	KCAOH +	14.5350	-12.5980	57.0870
1501400	KCAHCO3 +	1.7900	11.3300	101.0970
1501401	KCACO3 AQ	4.0300	3.1500	100.0890
1507320	KCASO4 AQ	1.4700	2.3090	136.1410
1505800	KCAHPO4 AQ	-0.2300	15.0850	136.0590
1505801	KCAPO4 -	3.1000	6.4590	135.0510
1505802	KCAH2PO4 +	-1.1200	20.9600	137.0670
1502700	KCAF +	3.7980	0.9400	59.0780
5001400	KNACO3 -	8.9110	1.2680	82.9990
5001401	KNAHCO3 AQ	0.0000	10.0800	84.0070
5007320	KNASO4 -	1.1200	0.7000	119.0510
5005800	KNAHPO4 -	0.0000	12.6360	118.9690
5002700	KNAF AQ	0.0000	-0.7900	41.9880
4107320	KKSO4 -	2.2500	0.8500	135.1630
4105800	KKHPO4 -	0.0000	12.6400	135.0810
303300	KALOH +2	11.8990	-4.9900	43.9880
303301	KAL(OH)2 +	0.0000	-10.1000	60.9960
303302	KAL(OH)4 -	44.0600	-23.0000	95.0110
302700	KALF +2	0.0000	7.0100	45.9790
302701	KALF2 +	20.0000	12.7500	64.9780
302702	KALF3 AQ	2.5000	17.0200	83.9760
302703	KALF4 -	0.0000	19.7200	102.9750
307320	KALSO4 +	2.1500	3.0200	123.0430

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Aqueous Complexes	**********	
307321	KAL(SO4)2 -	2.8400	4.9200	219.1040
303303	KAL(OH)3 AQ	0.0000	-16.0000	78.0030
2803300	KFEOH +	13.1990	-9.5000	72.8540
2803301	KFEOH3 -1	30.3000	-31.0000	106.8690
2807320	KFESO4 AQ	3.2300	2.2500	151.9080
2805800	KFEH2PO4 +	0.0000	22.2530	152.8340
2803302	KFEOH2 AQ	28.5650	-20.5700	89.8610
2805801	KFEHPO4 AQ	0.0000	15.9500	151.8260
2807300	KFE(HS)2 AQ	0.0000	8.9500	121.9900
2807301	KFE(HS)3 -	0.0000	10.9870	155.0620
2813300	KFEOH +2	10.3990	-2.1900	72.8540
2815800	KFEHPO4 +	-7.3000	17.7800	151.8260
2817320	KFESO4 +	3.9100	3.9200	151.9080
2811800	KFECL +2	5.6000	1.4800	91.3000
2811801	KFECL2 +	0.0000	2.1300	126.7530
2811802	KFECL3 AQ	0.0000	1.1300	162.2060
2813301	KFEOH2 +	0.0000	-5.6700	89.8610
2813302	KFEOH3 AQ	0.0000	-13.6000	106.8690
2813303	KFEOH4 -	0.0000	-21.6000	123.8760
2815801	KFEH2PO4 +2	0.0000	24.9800	152.8340
2812700	KFEF +2	2.6990	6.1990	74.8450
2812701	KFEF2 +	4.8000	10.8000	93.8430
2812702	KFEF3 AQ	5.3990	14.0000	112.8420
2817321	KFE(SO4)2 -	4.6000	5.4200	247.9700
2811410	KFE FULVATE	0.0000	9.3990	705.8470
2811420	KFE HUMATE	0.0000	9.3990	2055.8459
2813304	KFE2(OH)2+4	13.5000	-2.9500	145.7080
2813305	KFE3(OH)4+5	14.3000	-6.3000	235.5700
4407320	KLISO4 -	0.0000	0.6400	103.0000
8003300	KSROH +	14.4950	-13.1780	104.6270
1003300	KBAOH +	15.0950	-13.3580	154.3470
4701800	KMNCL +	0.0000	0.6070	90.3910
4701801	KMNCL2 AQ	0.0000	0.0410	125.8440
4701802	KMNCL3 -	0.0000	-0.3050	161.2970
4703300	KMNOH +	14.3990	-10.5900	161.2970
4703301	KMN(OH)3 -1	0.0000	-34.8000	105.9600
4702700	KMNF +	0.0000	0.8500	73.9360
4707320	KMNSO4 AQ	2.1700	2.2600	150.9990
4704920	KMN(NO3)2AQ	-0.3960	0.6000	178.9470
4701400	KMNHCO3 +	0.0000	11.6000	115.9550
4700020	KMNO4 -	176.6200	-127.8240	118.9350
4700021	KMNO4 -2	150.0200	-118.4400	118.9350
2301800	KCUCL2 -	-0.4200	5.5000	134.4520
2301801	KCUCL3 -2	0.2600	5.7000	169.9050

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Aqueous Complexes	**********	
2307300	KCU(S4)2 -3	0.0000	3.3900	320.0580
2307301	KCUS4S5 -3	0.0000	2.6600	352.1220
2301431	KCU ACETATE	0.0000	2.2400	122.5900
2301451	KCU GLYCINE	0.0000	8.6200	137.6100
2301452	KCU GLYCINE	0.0000	6.9700	201.1500
2301461	KCU SALICYL	0.0000	10.6400	199.6600
2301462	KCU SALICYL	0.0000	6.3000	263.2000
2301471	KCU GLUTAMA	0.0000	7.8500	208.6700
2301472	KCU GLUTAMA	0.0000	6.5500	272.2100
2301481	KCU PHTHALA	0.0000	3.4600	227.6700
2301482	KCU PHTHALA	0.0000	1.3700	291.2100
2311400	KCUCO3 AQ	0.0000	6.7300	123.5550
2311401	KCU(CO3)2-2	0.0000	9.8300	183.5640
2311800	KCUCL +	8.6500	0.4300	98.9990
2311801	KCUCL2 AQ	10.5600	0.1600	134.4520
2311802	KCUCL3 -	13.6900	-2.2900	169.9050
2311803	KCUCL4 -2	17.7800	-4.5900	205.3580
2312700	KCUF +	1.6200	1.2600	82.5440
2313300	KCUOH +	0.0000	-8.0000	80.5530
2313301	KCU(OH)2 AQ	0.0000	-13.6800	97.5600
2313302	KCU(OH)3 -	0.0000	-26.8990	114.5680
2313303	KCU(OH)4 -2	0.0000	-39.6000	131.5750
2313304	KCU2(OH)2+2	17.5390	-10.3590	161.1060
2317320	KCUSO4 AQ	1.2200	2.3100	159.6070
2317300	KCU(HS)3 -	0.0000	25.8990	162.7610
2311402	KCUHCO3 +	0.0000	13.0000	124.5630
2311410	KCU FULVATE	0.0000	6.1990	713.5460
2311420	KCU HUMATE	0.0000	6.1990	2063.5449
9501800	KZNCL +	7.7900	0.4300	100.8230
9501801	KZNCL2 AQ	8.5000	0.4500	136.2760
9501802	KZNCL3 -	9.5600	0.5000	171.7290
9501803	KZNCL4 -2	10.9600	0.1990	207.1820
9502700	KZNF +	2.2200	1.1500	84.3680
9503300	KZNOH +	13.3990	-8.9600	82.3770
9503301	KZN(OH)2 AQ	0.0000	-16.8990	99.3840
9503302	KZN(OH)3 -	0.0000	-28.3990	116.3920
9503303	KZN(OH)4 -2	0.0000	-41.1990	133.3990
9501804	KZNOHCL AQ	0.0000	-7.4800	117.8300
9507300	KZN(HS)2 AQ	0.0000	14.9400	131.5130
9507301	KZN(HS)3 -	0.0000	16.1000	164.5850
9507320	KZNSO4 AQ	1.3600	2.3700	161.4310
9507321	KZN(SO4)2-2	0.0000	3.2800	257.4930
9501300	KZNBR +	0.0000	-0.5800	145.2740
9501301	KZNBR2 AQ	0.0000	-0.9800	225.1780

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Aqueous	Complexes **********	
9503800	KZNI +	0.0000	-2.9100	192.2740
9503801	KZNI2 AQ	0.0000	-1.6900	319.1780
9501400	KZNHCO3 +	0.0000	12.4000	126.3570
9501401	KZNCO3 AQ	0.0000	5.3000	125.3790
9501402	KZN(CO3)2-2	0.0000	9.6300	185.3580
1601800	KCDCL +	0.5900	1.9800	147.8530
1601801	KCDCL2 AQ	1.2400	2.6000	183.3060
1601802	KCDCL3 -	3.9000	2.3990	218.7590
1602700	KCDF +	0.0000	1.1000	131.3980
1602701	KCDF2 AQ	0.0000	1.5000	150.3960
1601400	KCD(CO3)3-4	0.0000	6.2200	292.4280
1603300	KCDOH +	13.1000	-10.0800	129.4070
1603301	KCD(OH)2 AQ	0.0000	-20.3500	146.4140
1603302	KCD(OH)3 -	0.0000	-33.3000	163.4220
1603303	KCD(OH)4 -2	0.0000	-47.3500	180.4290
1603304	KCD2OH +3	10.8990	-9.3900	241.8074
1601803	KCDOHCL AQ	4.3550	-7.4040	164.8600
1604920	KCDNO3 +	-5.2000	0.3990	174.4040
1607320	KCDSO4 AQ	1.0800	2.4600	208.4610
1607300	KCDHS +	0.0000	10.1700	145.4720
1607301	KCD(HS)2 AQ	0.0000	16.5300	178.5430
1607302	KCD(HS)3 -	0.0000	18.7100	211.6150
1607303	KCD(HS)4 -2	0.0000	20.9000	244.6870
1601300	KCDBR +	-0.8100	2.1700	192.3040
1601301	KCDBR2 AQ	0.0000	2.8990	272.2080
1603800	KCDI +	-2.3700	2.1500	239.3040
1603801	KCDI2 AQ	0.0000	3.5900	366.2080
1601400	KCDHCO3 +	0.0000	12.4000	173.4170
1601401	KCDCO3 AQ	0.0000	5.3990	172.4090
1607321	KCD(SO4)2-2	0.0000	3.5000	208.4610
1601410	KCD FULVATE	0.0000	3.5000	762.3990
1601420	KCD HUMATE	0.0000	3.5000	2112.3989
6001800	KPBCL +	4.3800	1.6000	242.6430
6001801	KPBCL2 AQ	1.0800	1.8000	278.0960
6001802	KPBCL3 -	2.1700	1.6990	313.5490
6001803	KPBCL4 -2	3.5300	1.3800	349.0020
6001400	KPB(CO3)2-2	0.0000	10.6400	327.2080
6002700	KPBF +	0.0000	1.2500	226.1880
6002701	KPBF2 AQ	0.0000	2.5600	245.1860
6002702	KPBF3 -	0.0000	3.4200	264.1850
6002703	KPBF4 -2	0.0000	3.1000	283.1830
6003300	KPBOH +	0.0000	-7.7100	224.1970
6003301	KPB(OH)2 AQ	0.0000	-17.1200	241.2040
6003302	KPB(OH)3 -	0.0000	-28.0600	258.2120

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Aqueous	Complexes	**********
6003303	KPB2OH +3	0.0000	-6.3600	431.3870
6004920	KPBNO3 +	0.0000	1.1700	269.1940
6007320	KPBSO4 AQ	0.0000	2.7500	303.2510
6007300	KPB(HS)2 AQ	0.0000	15.2700	273.3330
6007301	KPB(HS)3 -	0.0000	16.5700	306.4050
6003304	KPB3(OH)4+2	26.5000	-23.8800	689.5990
6001300	KPBBR +	2.8800	1.7700	287.0940
6001301	KPBBR2 AQ	0.0000	1.4400	366.9980
6003800	KPBI +	0.0000	1.9400	334.0940
6003801	KPBI2 AQ	0.0000	3.1990	460.9980
6001401	KPBCO3 AQ	0.0000	7.2400	267.1990
6003305	KPB(OH)4 -2	0.0000	-39.6990	375.2190
6007321	KPB(SO4)2-2	0.0000	3.4700	399.3130
6001402	KPBHCO3 +	0.0000	13.2000	268.2070
5401300	KNIBR +	0.0000	0.5000	138.6140
5401800	KNICL +	0.0000	0.3990	94.1630
5402700	KNIF +	0.0000	1.3000	77.7080
5403300	KNIOH +	12.4200	-9.8600	75.7170
5403301	KNI(OH)2 AQ	0.0000	-19.0000	92.7240
5403302	KNI(OH)3 -	0.0000	-30.0000	109.7320
5407320	KNISO4 AQ	1.5200	2.2900	154.7710
5401801	KNICL2 AQ	0.0000	0.9600	129.6160
5401400	KNIHCO3 +	0.0000	12.4700	119.7270
5401401	KNICO3 AQ	0.0000	6.8700	118.7190
5401402	KNI(CO3)2-2	0.0000	10.1100	178.7280
5407321	KNI(SO4)2-2	0.0000	1.0200	250.8330
5401431	KNI ACETATE	0.0000	1.1200	117.7600
5401451	KNI GLYCINE	0.0000	6.1800	132.7800
5401452	KNI GLYCINE	0.0000	4.9600	191.4900
5401461	KNI SALICYL	0.0000	6.9500	194.8300
5401462	KNI SALICYL	0.0000	4.8000	253.5400
5401471	KNI GLUTAMA	0.0000	5.9000	203.8400
5401572	KNI GLUTAMA	0.0000	4.4400	262.5500
5401481	KNI PHTHALA	0.0000	2.1000	222.8400
201300	KAGBR AQ	0.0000	4.2400	187.7720
201301	KAGBR2 -	0.0000	7.2800	267.6760
201800	KAGCL AQ	-2.6800	3.2700	143.3210
201801	KAGCL2 -	-3.9300	5.2700	178.7740
201802	KAGCL3 -2	0.0000	5.2900	214.2270
201803	KAGCL4 -3	0.0000	5.5100	249.6790
202700	KAGF AQ	-2.8300	0.3600	126.8660
207300	KAGHS AQ	0.0000	14.0500	140.9390
207301	KAG(HS)2 -	0.0000	18.4500	174.0110
203800	KAGI AQ	0.0000	6.6000	234.7720

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Aqueous	Complexes	**********
203801	KAG12 -	0.0000	10.6800	361.6760
203300	KAGOH AQ	0.0000	-12.0000	124.8750
203301	KAG(OH)2 -	0.0000	-24.0000	141.8820
207320	KAGSO4 -	1.4900	1.2900	203.9290
204920	KAGNO3 AQ	0.0000	-0.2900	169.8720
204910	KAG(NO2)2 -	0.0000	2.2200	199.8790
201302	KAGBR3 -2	0.0000	8.7100	347.5800
203802	KAGI3 -2	-27.0300	13.3700	488.5810
203803	KAGI4 -3	0.0000	14.0800	615.4850
207302	KAG(S4)2 -3	0.0000	0.9910	364.3800
207303	KAGS4S5 -3	0.0000	0.6800	396.4440
207304	KAG(HS)S4-2	0.0000	10.4310	269.1960
201410	KAG FULVATE	0.0000	2.3990	757.8680
201420	KAG HUMATE	0.0000	2.3990	2107.8669
3300600	KH2ASO3 -	6.5600	-9.2280	124.9350
3300601	KHASO3 -2	14.1990	-21.3300	123.9270
3300602	KASO3 -3	20.2500	-34.7440	122.9190
3300610	KH4ASO3 +	0.0000	-0.3050	126.9510
3300611	KH2ASO4 -	-1.6900	-2.2430	140.9350
3300612	KHASO4 -2	-0.9200	-9.0010	139.9270
3300613	KASO4 -3	3.4300	-20.5970	138.9190
3301400	KHCO3 -	-3.6170	10.3300	61.0170
3301401	KH2CO3 AQ	-2.2470	16.6810	62.0250
3307320	KHSO4 -	4.9100	1.9870	97.0690
3302700	KHF AQ	3.4600	3.1690	20.0060
3302701	KHF2 -	4.5500	3.7490	39.0040
3302702	KH2F2 AQ	0.0000	6.7680	40.0120
3305800	KHPO4 -2	-3.5300	12.3460	95.9790
3305801	KH2PO4 -	-4.5200	19.5530	96.9870
3307300	KH2S AQ	-5.3000	6.9940	34.0790
3307301	KS -2	12.1000	-12.9180	32.0640
3301410	KH FULVATE	0.0000	4.2700	651.0080
3301420	KH HUMATE	0.0000	4.2700	2001.0070
8913300	KUOH +3	11.7150	-0.6560	255.0364
8913301	KU(OH)2 +2	17.7300	-2.2700	272.0437
8913302	KU(OH)3 +1	22.6450	-4.9350	289.0511
8913303	KU(OH)4 AQ	24.7600	-8.4980	306.0586
8913304	KU(OH)5 -1	27.5750	-13.1200	323.0659
8912700	KUF +3	5.0500	8.6590	257.0274
8912701	KUF2 +2	7.2000	14.4570	276.0258
8912702	KUF3 +1	7.1500	19.1150	295.0242
8912703	KUF4 AQ	4.6000	23.6400	314.0226
8912704	KUF5 -1	4.8500	25.2380	333.0210
8912705	KUF6 -2	3.3000	27.7180	352.0194

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Aqueous	Complexes	**********
8911800	KUCL +3	9.9330	1.3380	273.4820
8917320	KUSO4 +2	3.7000	5.4610	334.0906
8917321	KU(SO4)2 AQ	7.6000	9.7490	430.1522
8915800	KUHPO4 +2	7.5000	24.4430	334.0084
8915801	KU(HPO4)2AQ	1.7000	46.8330	429.9877
8915802	KU(HPO4)3-2	-7.8000	67.5540	525.9671
8915803	KU(HPO4)4-4	-26.5000	88.4830	621.9465
8933300	KUO2OH +1	10.2160	-5.0900	287.0352
8933301	KUO2)2OH2+2	10.2300	-5.6450	574.0703
8933302	KUO2)3OH5+1	25.0750	-15.5930	895.1203
8931400	KUO2CO3 AQ	0.8400	10.0710	330.0372
8931401	KUO2CO3)2-2	3.4800	17.0080	390.0465
8931402	KUO2CO3)3-4	-8.7800	21.3840	450.0559
8932700	KUO2F +1	-0.4500	5.1050	289.0262
8932701	KUO2F2 AQ	-0.9000	8.9200	308.0246
8932702	KUO2F3 -1	-0.8500	11.3640	327.0230
8932703	KUO2F4 -2	-1.1000	12.6070	346.0214
8931800	KUO2CL +1	1.2330	0.2200	305.4808
8937320	KUO2SO4 AQ	5.1000	2.7090	366.0894
8937321	KUO2SO4)2-2	6.1000	4.1830	462.1510
8935800	KUO2HPO4 AQ	-2.1000	20.8140	366.0072
8935801	KUO2HPO4)2	-11.3990	42.9880	461.9865
8935802	KUO2H2PO4+1	-3.7000	22.6430	367.0151
8935803	KUO2H2PO4)2	-16.5000	44.7000	464.0020
8935804	KUO2H2PO4)3	-28.6000	66.2450	560.9890
8937700	KUO2H3SIO4	0.0000	-2.4000	365.1350
7317300	KS2 -2	11.4000	-14.5280	64.1280
7317301	KS3 -2	10.4000	-13.2820	96.1920
7317302	KS4 -2	9.7000	-9.8290	128.2360
7317303	KS5 -2	9.3000	-9.5950	160.3200
7317304	KS6 -2	0.0000	-9.8810	192.3840
9003300	VOH +	0.0000	-5.6400	67.9470
9013300	VOH +2	9.3500	-2.3000	67.9470
9013301	V(OH)2 +1	0.0000	-5.8300	84.9550
9013302	V(OH)3 AQ	0.0000	-11.0200	101.9620
9017320	VSO4 +1	0.0000	1.4400	146.9980
9013303	V2(OH)3 +3	0.0000	-7.5000	152.9020
9013304	V2(OH)2 +4	0.0000	-3.7500	135.8950
9023300	V(OH)3 +1	0.0000	-5.8700	101.9620
9023301	H2V2O4 +2	0.0000	-6.4400	167.8940
9022700	VOF +	1.9000	3.3400	85.9370
9022701	VOF2 AQ	3.5000	5.7400	104.9350
9022702	VOF3 -1	4.9000	7.5000	123.9330
9022703	VOF4 -2	6.4000	8.1100	142.9310

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Aqueous Complexes	**********	
9027320	VOSO4 AQ	3.7200	2.4500	162.9970
9021800	VOCL +1	0.0000	0.0200	102.3920
9033300	H3VO4 AQ	10.6300	-3.3000	117.9620
9033301	H2VO4 -1	11.3300	-7.0900	116.9540
9033302	HVO4 -2	14.9300	-15.1500	115.9460
9033303	VO4 -3	19.5300	-28.4000	114.9380
9030020	V2O7 -4	0.0000	-29.0800	213.8760
9030021	HV2O7 -3	0.0000	-16.3200	214.8840
9030022	H3V2O7 -1	0.0000	-3.7900	216.9000
9030023	V3O9 -3	0.0000	-15.8800	296.8150
9030024	V4O12 -4	0.0000	-20.7900	395.7530
9030025	V10O28 -6	0.0000	-17.5300	957.3830
9030026	HV10O28 -5	21.5200	-11.3500	958.3910
9030027	H2V10O28 -4	0.0000	-7.7100	959.3990
9032700	VO2F AQ	0.0000	3.1200	101.9370
9032701	VO2F2 -1	0.0000	5.6700	120.9350
9032702	VO2F3 -2	0.0000	6.9700	139.9330
9032703	VO2F4 -3	0.0000	7.0700	158.9310
9037320	VO2SO4 -1	0.0000	1.7100	178.9960
9034920	VO2NO3 AQ	0.0000	-0.4300	144.9440
8703300	TlOH AQ	13.9350	-13.1717	221.3773
8702700	TlF AQ	0.0000	-0.4251	223.3684
8701800	TlCl AQ	-1.1470	0.6824	239.8230
8701801	TlCl2-1	0.0000	0.2434	275.2760
8701300	TlBr AQ	-2.4610	0.9477	284.2740
8701301	TlBr2-1	2.9980	0.9719	364.1780
8701302	TlBrCl-1	0.0000	0.8165	319.7270
8703800	TlI AQ	0.0000	1.4279	331.2745
8703801	TlI2-1	0.0000	1.8588	458.1790
8703802	TlIBr-1	0.0000	2.1850	411.1785
8707320	TlSO4-1	-0.2200	1.3853	300.4276
8704920	TlNO3 AQ	-0.6500	0.3665	266.3749
8704910	TlNO2 AQ	0.0000	0.9969	250.3755
8707300	TlHS AQ	0.0000	1.8178	237.4379
8707301	Tl2HS+1	0.0000	7.6979	441.8079
8707302	Tl2OH(HS)3-	0.0000	1.0044	524.9510
8707303	Tl2(OH)2(HS	0.0000	-11.0681	508.8904
8713300	Tl+3	0.0000	4.7424	204.3700
8713301	TlOH+2	0.0000	3.5770	221.3773
8713302	Tl(OH)2+1	0.0000	2.1183	238.3846
8711800	TlCl+2	0.0000	12.2342	239.8230
8711801	TlCl2+1	0.0000	18.0402	275.2760
8711802	TlCl3 AQ	0.0000	21.4273	310.7290
8711803	TlCl4-1	0.0000	24.2281	346.1820

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Aqueous Complexes	**********	
8711300	TlBr+2	0.0000	14.2221	284.2740
8711301	TLBr2+1	0.0000	21.5761	364.1780
8711302	TlBr3 AQ	0.0000	27.0244	444.0820
8711303	TlBr4-1	0.0000	31.1533	523.9860
8713800	Tl14-1	0.0000	34.7596	711.9880
8714920	TlNO3+2	0.0000	7.0073	266.3749
8713303	Tl(OH)4-1	0.0000	-10.2545	272.3992
8711804	TlOHCl+1	0.0000	10.6290	256.8303
3307601	Se-2	11.5000	-14.9529	78.9600
3307600	H2Se	0.8000	3.8115	80.9758
4707600	MnSe	0.0000	-6.7435	133.8980
207600	Ag2Se	0.0000	34.0677	294.6960
207601	AgOH(Se)2-4	0.0000	-18.6237	282.7953
3307611	SeO3-2	1.2800	-7.3005	126.9582
3307610	H2SeO3	1.6900	2.5728	128.9740
2817610	FeHSeO3+2	0.0000	1.8618	183.8131
207610	AgSeO3-1	0.0000	-5.5985	234.8262
207611	Ag(SeO3)2-3	0.0000	-10.9933	361.7844
1607610	Cd(SeO3)2-2	0.0000	-11.1890	366.3264
3307620	HSeO4-1	4.2000	1.9058	143.9655
4707620	MnSeO4	3.4600	2.4188	197.8956
2007620	CoSeO4	2.9100	2.7120	201.8908
5407620	NiSeO4	3.5000	2.6387	201.6576
1607620	CdSeO4	0.0000	2.2415	255.3676
9507620	ZnSeO4	0.0000	2.2019	208.3376
9507621	Zn(SeO4)2-2	0.0000	-0.0704	351.2952
3600000	Hg (aq)	-16.6050	6.9316	200.5900
3613300	Hg+2	-11.0600	6.0970	200.5900
3611301	HgBr+	0.0000	15.8347	280.4940
3611302	HgBr2 (aq)	-30.8320	23.6065	360.3980
3611303	HgBr3-1	0.0000	25.7857	440.3020
3611304	HgBr4-2	0.0000	27.0633	520.2060
3611305	HgBrCl (aq)	0.0000	22.0145	315.9470
3611306	HgBrI (aq)	0.0000	27.1212	407.3985
3611307	HgBrI3-2	0.0000	34.2135	661.2075
3611308	HgBr2I2-2	0.0000	32.3994	614.2070
3611309	HgBr3I-2	0.0000	30.1528	567.2065
3613301	HgBrOH (aq)	0.0000	11.5980	297.5013
3611800	HgCl+1	0.0000	12.8500	236.0430
3611801	HgCl2 (aq)	0.0000	19.2203	271.4960
3811802	HgCl3-1	0.0000	20.1226	306.9490
3611803	HgCl4-2	0.0000	20.5338	342.4020
3611804	HgClI (aq)	0.0000	25.3532	362.9475
3611805	HgClOH (aq)	-12.4820	9.3170	253.0503

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Aqueous	Complexes	**********
3612701	HgF+1	0.0000	8.0848	219.5884
3613801	HGI+1	0.0000	18.8949	327.4945
3613802	HgI2 (aq)	-44.5220	30.1081	454.3990
3613803	HgI3-1	-47.9430	33.7935	581.3035
3613804	HgI4-2	0.0000	35.7858	708.2080
3614900	HgNH3+2	0.0000	5.6139	217.6204
3614901	Hg(NH3)2+2	0.0000	5.0341	234.6508
3614902	Hg(NH3)3+2	0.0000	-3.2493	251.6812
3614903	Hg(NH3)4+2	0.0000	-11.7307	268.7116
3614920	HgNO3+1	0.0000	6.4503	262.5949
3614921	Hg(NO3)2 (a	0.0000	4.7791	324.5998
3613302	HgOH+1	0.0000	2.6974	217.5973
3613303	Hg(OH)3-1	0.0000	-15.0042	251.6119
3617300	HgS2-2	0.0000	31.2398	264.7100
3617301	Hg(HS)2 (aq	0.0000	43.8178	266.7258
3617320	HgSO4 (aq)	0.0000	7.4911	296.6476
3611401	HgCH3NH2+2	0.0000	29.3846	231.6472
3611402	Hg(CH3NH2)2	-87.3400	53.2132	262.7044
2113300	CR+3	-20.1400	9.6200	51.9960
2113301	CR(OH)+2	0.0000	5.6200	69.0033
2110020	CR(OH)3 AQ	0.0000	-7.1300	103.0179
2110021	CR(OH)4-	0.0000	-18.1500	20.0252
2113304	CRO2-	0.0000	-17.7456	83.9948
2111300	CRBR+2	-11.2110	7.5519	131.9000
2111800	CRCL+2	-13.8470	9.3683	87.4490
2111801	CRCL2 +	-9.3740	8.6580	122.9020
2111802	CROHCL2 AQ	0.0000	2.9627	139.9093
2112700	CRF+2	-16.7890	14.5424	70.9944
2113800	CRI+2	0.0000	4.8289	178.9005
2114900	CR(NH3)6+3	0.0000	-32.5709	154.1784
2114901	CRNH3)5OH+2	0.0000	-30.2759	154.1553
2114902	CCRNH3)4OH2	0.0000	-29.8574	154.1322
2114903	TCRNH3)4OH2	0.0000	-30.5537	154.1322
2114904	CRNH3)6CL+2	0.0000	-31.7932	189.6314
2114905	CRNH3)6BR+2	0.0000	-31.8870	234.0824
2114906	CRNH3)6I +2	0.0000	-32.0080	281.0829
2114920	CRNO3 +2	-15.6400	8.2094	114.0009
2115800	CRH2PO4 +2	0.0000	31.9068	148.9832
2117320	CRSO4 +	-12.6200	10.9654	148.0536
2117321	CROHSO4 AQ	0.0000	8.2754	165.0609
2117322	CR2OH2SO4)S	0.0000	14.5278	330.1218
2117323	CR2OH2SO4+2	0.0000	16.1550	234.0642
2117324	CR2OH2SO42	0.0000	17.9288	330.1218

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Aqueous Complexes	**********	
2123300	HCRO4 -	0.9000	6.5089	117.0015
2123301	H2CRO4 AQ	0.0000	5.6513	118.0094
2123302	CR2O7 -2	-2.9950	14.5571	215.9878
2121800	CRO3CL -	0.0000	7.3086	135.4472
2125800	CRO3H2PO4-	0.0000	29.3634	196.9814
2125801	CRO3HPO4-2	0.0000	26.6806	195.9735
2127320	CRO3SO4-2	0.0000	8.9937	196.0518
5002120	NACRO4-	0.0000	0.6963	138.9834
4102120	KCRO4-	0.0000	0.7990	155.0919
3301431	KH ACETATE	0.0000	4.7600	60.0600
3301441	KH TARTRAT	0.0000	4.1600	149.1000
3301442	KH TARTRAT	0.0000	2.5200	150.1100
3301451	KH GLYCINE	0.0000	9.7800	75.0800
3301452	KH GLYCINE	0.0000	2.3500	76.0900
3301461	KH SALICYL	0.0000	13.4000	137.1300
3301462	KH SALICYL	0.0000	3.0000	138.1400
3301471	KH GLUTAMA	0.0000	9.9500	146.1400
3301472	KH GLUTAMA	0.0000	4.2800	147.1500
3301481	KH PHTHALA	0.0000	5.4000	165.1400
3301482	KH PHTHALA	0.0000	3.1400	166.1500
1601431	KCD ACETATE	0.0000	1.7000	171.4600
1601441	KCD TARTRAT	0.0000	3.9000	260.5000
1601451	KCD GLYCINE	0.0000	4.8000	186.4800
1601452	KCD GLYCINE	0.0000	4.0300	260.5500
1601471	KCD GLUTAMA	0.0000	4.7800	257.5400
1601472	KCD GLUTAMA	0.0000	2.7800	402.6700
1601481	KCD PHTHALA	0.0000	2.5000	276.5400
6001431	KPB ACETATE	0.0000	2.1000	266.2600
6001441	KPB TARTRAT	0.0000	3.7800	355.3000
6001451	KPB GLYCINE	0.0000	5.4700	281.2800
6001452	KPB GLYCINE	0.0000	3.3900	355.3500
1001431	KBA ACETATE	0.0000	0.4100	196.4100
1001441	KBA TARTRATE	0.0000	2.5400	285.4500
1001451	KBA GLYCINE	0.0000	0.7700	211.4300
1001461	KBA SALICYL	0.0000	0.2100	273.4800
1001471	KBA GLUTAMA	0.0000	1.2800	282.4900
1001481	KBA PHTHALA	0.0000	2.3300	301.4900
201431	KAG ACETATE	0.0000	0.7300	166.9300
201432	KAG ACETATE	0.0000	-0.0900	225.9800
201451	KAG GLYCINE	0.0000	3.5100	181.9500
201452	KAG GLYCINE	0.0000	3.3800	256.0200
2111431	KCR ACETATE	0.0000	1.8000	111.0600
2111432	KCR ACETATE	0.0000	2.9200	170.1100
2111451	KCR GLYCINE	0.0000	8.4000	126.0800

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Aqueous Complexes	**********	
2111452	KCR GLYCINE	0.0000	6.4000	200.1500
2111453	KCR GLYCINE	0.0000	5.7000	274.2200
2111481	KCR PHTHALA	0.0000	5.5200	216.1400
2111482	KCR PHTHALA	0.0000	4.8000	380.2700
2111483	KCR PHTHALA	0.0000	2.4800	544.4000
8711441	KT1 TARTRAT	0.0000	1.3900	352.4800
3601451	KHg GLYCINE	0.0000	10.8000	274.6800
3601452	KHg GLYCINE	0.0000	20.0000	348.7500
	**********	Solid Species	**********	
2089100	URANINITE	18.6300	4.7000	270.0278
2089101	UO2 (AM)	26.2300	-0.9340	270.0278
3089100	U409 (C)	101.2350	3.3840	1096.1106
3089101	U308 (C)	116.0200	-21.1070	842.0822
8089100	USIO4 (C)	14.5480	7.6200	330.1121
4289100	UF4 (C)	18.9000	18.6060	314.0226
4289101	UF4.2.5H2O	0.5880	27.5700	359.0606
7089100	UHPO4)2,4H2O	-3.8400	51.5840	502.0486
7015000	NINGYOITE	2.2700	53.9060	504.0822
2089300	UO3 (C)	19.3150	-7.7190	286.0272
2089301	GUMMITE	23.0150	-10.4030	286.0272
2089302	B-UO2(OH)2	13.7300	-5.5440	304.0424
2089303	SCHOEPITE	12.0450	-5.4040	322.0576
5089300	RUTHERFORDIN	1.4400	14.4390	330.0370
7089300	(UO2)3(PO4)2	-94.9000	49.0370	1000.0262
7089301	H-AUTUNITE	3.6000	47.9310	732.0144
7050000	NA-AUTUNITE	0.4600	47.4090	775.9780
7041000	K-AUTUNITE	-5.8600	48.2440	808.2024
7049000	URAMPHITE	-9.7000	51.7490	766.0756
7046000	SALEEITE	20.1800	43.6460	754.3104
7015001	AUTUNITE	14.3400	43.9270	770.0784
7080000	SR-AUTUNITE	13.0500	44.4570	817.6184
7010000	URANOCIRCITE	10.1000	44.6310	867.3384
7028000	BASSETITE	19.9000	44.4850	785.8454
7023100	TORBERNITE	15.9000	45.2790	793.5444
7060000	PRZHEVALSKIT	11.0000	44.3650	937.1883
8015000	URANOPHANE	0.0000	-17.4900	766.5176
5189300	UO2NO3)2	20.1400	-12.3690	394.0380
5189301	UO2NO3.2H2O	6.0600	-4.8510	430.0690
5189302	UO2NO3.3H2O	2.4050	-3.6420	448.0840

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Solid Species	**********	
5189303	UO2NO3.6H2O	-4.7700	-2.3000	502.1300
2003000	ALOH3(A)	27.0450	-10.3800	78.0073
6003000	ALOHSO4	0.0000	3.2300	140.0505
6003001	AL4(OH)10SO4	0.0000	-22.7000	374.0616
6041000	ALUM K	-7.2200	5.1700	438.3597
6041001	ALUNITE	-3.9180	1.3460	414.2141
6015000	ANHYDRITE	3.7690	4.6370	136.1416
5015000	ARAGONITE	2.6150	8.3600	100.0894
5046000	ARTINITE	28.7420	-9.6000	196.6941
4210000	BAF2	-1.0000	5.7600	175.3368
6010000	BARITE	-6.2800	9.9760	233.4016
2003001	BOEHMITE	28.1300	-8.5780	59.9884
2046000	BRUCITE	25.8400	-16.7920	58.3268
5015001	CALCITE	2.5850	8.4750	100.0894
6080000	CELESTITE	0.4700	6.4650	183.6816
2077000	CHALCEDONY	-4.6150	3.5230	60.0848
8646000	CHRYSOTILE	52.4850	-32.1880	277.1349
8246000	CLINOENSTITE	20.0150	-11.3380	100.3964
2077001	CRISTOBALITE	-5.5000	3.5870	60.0848
2003002	DIASPORE	24.6300	-6.8730	59.9884
8215000	DIOPSIDE	32.2800	-19.8860	216.5608
5015002	DOLOMITE	8.2900	17.0000	184.4108
6046000	EPSOMITE	-2.8200	2.1400	246.4807
8646003	SEPIOLITE(C)	27.2680	-15.9130	323.9313
2028100	FERRIHYDRITE	0.0000	-4.8910	104.8692
2028101	FE3(OH)8	0.0000	-20.2220	297.6002
4128100	FEOH)2.7CL.3	0.0000	3.0400	110.4029
1028000	FES PPT	0.0000	3.9150	85.9110
6028100	FE2(SO4)3	59.1200	-3.5800	395.8788
7015002	FCO3APATITE	-39.3900	114.4000	967.3670
4215000	FLUORITE	-4.7100	10.9600	78.0768
8046000	FORSTERITE	48.5100	-28.2980	236.8234
2003003	GIBBSITE (C)	22.8000	-8.7700	78.0037
2028102	GOETHITE	14.4800	-0.5000	86.8536
8628000	GREENALITE	0.0000	-20.8100	365.7393
1028001	GREIGITE	0.0000	45.0350	289.7970
6015001	GYPSUM	-0.2610	4.8480	172.1722
4150000	HALITE	-0.9180	-1.5820	58.4428
3028100	HEMATITE	30.8450	4.0080	155.6919
5015003	HUNTITE	25.7600	29.9680	353.0536
5046001	HYDRMAGNESIT	52.2100	8.7660	467.6736
6050000	JAROSITE NA	36.1800	11.2000	478.6978
6041002	JAROSITE K	31.2800	14.8000	494.8100
6028101	JAROSITE H	55.1500	12.1000	480.7320

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Solid Species	**********	
1028002	MACKINAWITE	0.0000	4.6480	87.9110
8450000	MAGADIITE	0.0000	14.3000	532.6521
3028101	MAGHEMITE	0.0000	-6.3860	159.6922
5046002	MAGNESITE	6.1690	8.0290	84.3214
3028000	MAGNETITE	50.4600	-3.7370	231.5386
6028000	MELANTERITE	-2.8600	2.4700	278.0157
6050001	MIRABILITE	-18.9870	1.1140	322.1942
3050000	NATRON	-15.7450	1.3110	286.1420
5046003	NESQUEHONITE	5.7890	5.6210	138.3673
8646001	PHLOGOPITE	86.3600	-66.3000	417.2863
1028003	PYRITE	-11.3000	18.4790	119.9750
2077002	QUARTZ	-6.2200	4.0060	60.0848
8646004	SEPIOLITE(A)	0.0000	-18.7800	323.9308
5028000	SIDERITE	5.3280	10.5500	115.8564
2077003	SIO2(A,GL)	-4.4400	3.0180	60.0848
2077004	SIO2(A,PT)	-3.9100	2.7100	60.0848
4280000	SRF2	-1.2500	8.5400	125.6168
7028100	STRENGITE	2.0300	26.4000	186.8490
5080000	STRONTIANITE	0.6900	9.2500	147.6294
8646002	TALC	35.0050	-23.0550	379.2888
6050002	THENARDITE	0.5720	0.1790	142.0412
5050001	THERMONATR	2.8020	-0.1250	124.0043
8215001	TREMOLITE	96.6150	-56.5460	812.4096
7028001	VIVIANITE	0.0000	36.0000	501.6062
5010000	WITHERITE	-0.3600	8.5850	197.3494
2047000	PYROLUSITE	29.1800	-15.8610	86.9368
2047001	BIRNESSITE	0.0000	-18.0910	86.9368
2047002	NSUTITE	0.0000	-17.5040	86.9368
3047100	BIXBYITE	15.2450	0.6110	157.8742
3047000	HAUSMANNITE	80.1400	-61.5400	228.8116
2047003	PYROCROITE	22.5900	-15.0880	88.9528
2047100	MANGANITE	0.0000	0.2380	87.9448
5047000	RHODOCHROSIT	2.0790	10.4100	114.9474
4147000	MNCL2, 4H2O	-17.3800	-2.7100	197.9052
1047000	MNS GREEN	5.7900	-3.8000	87.0020
6047000	MNSO4	15.4800	-2.6690	150.9996
6047100	MN2(SO4)3	39.0600	5.7110	398.0608
7047000	MN3(PO4)2	-2.1200	23.8270	354.7568
3041000	A-CRYPTOMELN	0.0000	0.0000	775.7382
3010000	HOLLANDITE	0.0000	0.0000	817.4214
3015000	TODOROKITE	0.0000	0.0000	592.4641
3044000	LITHIOPHORIT	0.0000	0.0000	1953.3934
3015001	RANCIEITE	0.0000	0.0000	466.1930
23000	CU METAL	-17.1300	8.7600	63.5460

Species D Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Solid Species	**********	
4123000	NANTOKITE	-9.9800	6.7600	98.9990
4223000	CUF	12.3700	-7.0800	82.5444
2023000	CUPRITE	-6.2450	1.5500	143.0914
1023000	CHALCOCITE	-49.3500	34.6190	159.1560
1023001	DJURLEITE	-47.8810	33.9200	154.9620
1023002	ANILITE	-43.5350	31.8780	143.2695
1023003	BLAUBLEI II	0.0000	27.2790	121.0284
1023100	BLAUBLEI I	0.0000	24.1620	101.9646
1023101	COVELLITE	-24.0100	23.0380	95.6100
6023000	CU2SO4	4.5600	1.9500	223.1536
3023000	CUPROUSFERIT	3.8000	8.9200	151.3918
4123100	MELANOTHALLI	12.3200	-3.7300	134.4520
5023100	CUCO3	0.0000	9.6300	123.5552
4223100	CUF2	13.3200	0.6200	101.5428
4223101	CUF2, 2H2O	3.6500	4.5500	137.5732
2023100	CU(OH)2	15.2500	-8.6400	97.5606
4123101	ATACAMITE	18.6900	-7.3400	213.5669
5123100	CU2(OH)3NO3	17.3500	-9.2400	240.1188
6023100	ANTLERITE	0.0000	-8.2900	354.7248
6023101	BROCHANTITE	0.0000	-15.3400	452.2854
6023102	LANGITE	39.6100	-16.7900	470.3006
2023101	TENORITE	15.2400	-7.6200	79.5454
6023103	CUOCUSO4	35.5750	-11.5300	239.1490
7023100	CU3(PO4)2	0.0000	36.8500	380.5808
7023101	CU3(PO4)2,3W	0.0000	35.1200	434.6264
6023104	CUSO4	18.1400	-3.0100	159.6036
6023105	CHALCANTHITE	-1.4400	2.6400	249.6796
2023102	DIOPTASE	8.9600	-6.5000	157.6449
3023100	CUPRICFERIT	38.6900	-5.8800	239.2376
1023102	CHALCOPYRITE	-35.4800	35.2700	183.5130
4023000	CUBR	-13.0800	8.2100	143.4500
4323000	CUI	-20.1400	11.8900	190.4505
95000	ZN METAL	36.7800	-25.7570	65.3800
4195000	ZNCL2	17.4800	-7.0300	136.2860
5095000	SMITHSONITE	4.3600	10.0000	125.3892
5095001	ZNCO3, 1H2O	0.0000	10.2600	143.4044
4295000	ZNF2	13.0800	1.5200	103.3768
2095000	ZN(OH)2 (A)	0.0000	-12.4500	99.3946
2095001	ZN(OH)2 (C)	0.0000	-12.2000	99.3946
2095002	ZN(OH)2 (B)	0.0000	-11.7500	99.3946
2095003	ZN(OH)2 (G)	0.0000	-11.7100	99.3946
2095004	ZN(OH)2 (E)	0.0000	-11.5000	99.3946
4195001	ZN2(OH)3CL	0.0000	-15.2000	217.2349
4195002	ZN5(OH)8CL2	0.0000	-38.5000	533.8644

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Solid Species	**********	
6095000	ZN2(OH)2SO4	0.0000	-7.5000	260.8322
6095001	ZN4(OH)6SO4	0.0000	-28.4000	459.6214
5195000	ZNNO3)2,6H2O	-5.5100	-3.4400	297.4810
2095005	ZNO(ACTIVE)	0.0000	-11.3100	81.3794
2095006	ZINCITE	21.8600	-11.1400	81.3794
6095002	ZN3O(SO4)2	62.0000	-19.0200	404.2546
7095000	ZN3(PO4),4W	0.0000	32.0400	458.1436
1095000	ZNS (A)	-3.6700	9.0520	97.4400
1095001	SPHALERITE	-8.2500	11.6180	97.4400
1095002	WURTZITE	-5.0600	9.6820	97.4400
8295000	ZNSIO3	18.2700	-2.9300	141.4637
8095000	WILLEMITE	33.3700	-15.3300	220.8431
6095003	ZINCOSITE	19.2000	-3.0100	161.4376
6095004	ZNSO4, 1H2O	10.6400	0.5700	179.4528
6095005	BIANCHITE	0.1600	1.7650	269.5288
6095006	GOSLARITE	-3.3000	1.9600	287.5440
4095000	ZNBR2, 2H2O	7.5100	-5.2100	261.2184
4395000	ZNI2	13.4400	-7.2300	319.1890
16000	CD METAL	18.0000	-13.4900	112.4100
16001	GAMMA CD	18.1400	-13.5900	112.4100
5016000	OTAVITE	0.5800	13.7400	172.4192
4116000	CDCL2	4.4700	0.6800	183.3160
4116001	CDCL2, 1H2O	1.8200	1.7100	201.3312
4116002	CDCL2,2.5H2O	-1.7100	1.9400	228.3536
4216000	CDF2	9.7200	2.9800	150.4068
2016000	CD(OH)2 (A)	20.7700	-13.7300	146.4246
2016001	CD(OH)2 (C)	0.0000	-13.6500	146.4246
4116003	CDOHCL	7.4070	-3.5200	164.8703
6016000	CD3(OH)4SO4	0.0000	-22.5600	501.3168
6016001	CD3OH2(SO4)2	0.0000	-6.7100	563.3598
6016002	CD4(OH)6SO4	0.0000	-28.4000	647.7414
2016002	MONTEPONITE	24.7600	-15.1200	128.4094
7016000	CD3(PO4)2	0.0000	32.6000	527.1728
8216000	CDSIO3	16.6300	-9.0600	188.4937
6016003	CDSO4	14.7400	0.1000	208.4676
6016004	CDSO4, 1H2O	7.5200	1.6570	226.4828
6016005	CDSO4,2.7H2O	4.3000	1.8730	256.3879
1016000	GREENOCKITE	-16.3600	15.9300	144.4700
4016000	CDBR2, 4H2O	-7.2300	2.4200	344.2788
4316000	CDI2	-4.0800	3.6100	366.2190
60000	PB METAL	-0.4000	-4.2700	207.2000
4160000	COTUNNITE	-5.6000	4.7700	278.1060
4160001	MATLOCKITE	-7.9500	9.4300	261.6514
4160002	PHOSGENITE	0.0000	19.8100	545.3152

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Solid Species	**********	
5060000	CERRUSITE	-4.8600	13.1300	267.2092
4260000	PBF2	0.7000	7.4400	245.1968
2060000	MASSICOT	16.7800	-12.9100	223.1994
2060001	LITHARGE	16.3800	-12.7200	223.1994
2060002	PBO, .3H2O	0.0000	-12.9800	229.1444
5060001	PB2OCO3	11.4600	0.5000	490.4086
6060000	LARNAKITE	6.4400	0.2800	526.4570
6060001	PB3O2SO4	20.7500	-10.4000	749.6564
6060002	PB4O3SO4	35.0700	-22.1000	972.8558
7060001	CLPYROMORPH	0.0000	84.4300	1356.3672
7060002	HXYPYROMORPH	0.0000	62.7900	1337.9215
2095002	ZN(OH)2 (B)	0.0000	-11.7500	99.3946
2095003	ZN(OH)2 (G)	0.0000	-11.7100	99.3946
2095004	ZN(OH)2 (E)	0.0000	-11.5000	99.3946
4195001	ZN2(OH)3CL	0.0000	-15.2000	217.2349
4195002	ZN5(OH)8CL2	0.0000	-38.5000	533.8644
6095000	ZN2(OH)2SO4	0.0000	-7.5000	260.8322
6095001	ZN4(OH)6SO4	0.0000	-28.4000	459.6214
5195000	ZNNO3)2,6H2O	-5.5100	-3.4400	297.4810
2095005	ZNO(ACTIVE)	0.0000	-11.3100	81.3794
2095006	ZINCITE	21.8600	-11.1400	81.3794
6095002	ZN3O(SO4)2	62.0000	-19.0200	404.2546
7095000	ZN3(PO4),4W	0.0000	32.0400	458.1436
1095000	ZNS (A)	-3.6700	9.0520	97.4400
1095001	SPHALERITE	-8.2500	11.6180	97.4400
1095002	WURTZITE	-5.0600	9.6820	97.4400
8295000	ZNSIO3	18.2700	-2.9300	141.4637
8095000	WILLEMITE	33.3700	-15.3300	220.8431
6095003	ZINCOSITE	19.2000	-3.0100	161.4376
6095004	ZNSO4, 1H2O	10.6400	0.5700	179.4528
6095005	BIANCHITE	0.1600	1.7650	269.5288
6095006	GOSLARITE	-3.3000	1.9600	287.5440
4095000	ZNBR2, 2H2O	7.5100	-5.2100	261.2184
4395000	ZNI2	13.4400	-7.2300	319.1890
16000	CD METAL	18.0000	-13.4900	112.4100
16001	GAMMA CD	18.1400	-13.5900	112.4100
5016000	OTAVITE	0.5800	13.7400	172.4192
4116000	CDCL2	4.4700	0.6800	183.3160
4116001	CDCL2, 1H2O	1.8200	1.7100	201.3312
4116002	CDCL2,2.5H2O	-1.7100	1.9400	228.3536
4216000	CDF2	9.7200	2.9800	150.4068
2016000	CD(OH)2 (A)	20.7700	-13.7300	146.4246
2016001	CD(OH)2 (C)	0.0000	-13.6500	146.4246
4116003	CDOHCL	7.4070	-3.5200	164.8703

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Solid Species	**********	
6016000	CD3(OH)4SO4	0.0000	-22.5600	501.3168
6016001	CD3OH2(SO4)2	0.0000	-6.7100	563.3598
6016002	CD4(OH)6SO4	0.0000	-28.4000	647.7414
2016002	MONTEPONITE	24.7600	-15.1200	128.4094
7016000	CD3(PO4)2	0.0000	32.6000	527.1728
8216000	CDSIO3	16.6300	-9.0600	188.4937
6016003	CDSO4	14.7400	0.1000	208.4676
6016004	CDSO4, 1H2O	7.5200	1.6570	226.4828
6016005	CDSO4,2.7H2O	4.3000	1.6730	256.3879
1016000	GREENOCKITE	-16.3600	15.9300	144.4700
4016000	CDBR2, 4H2O	-7.2300	2.4200	344.2788
4316000	CDI2	-4.0800	3.6100	366.2190
60000	PB METAL	-0.4000	-4.2700	207.2000
4160000	COTUNNITE	-5.6000	4.7700	278.1060
4160001	MATLOCKITE	-7.9500	9.4300	261.6514
4160002	PHOSGENITE	0.0000	19.8100	545.3152
5060000	CERRUSITE	-4.8600	13.1300	267.2092
4260000	PBF2	0.7000	7.4400	245.1968
2060000	MASSICOT	16.7800	-12.9100	223.1994
5023102	AZURITE	23.7700	16.9200	344.6716
3006000	ARSENOLITE	-14.3300	2.8010	395.6824
3006001	CLAUDETITE	-13.2900	3.0650	395.6824
4306000	ASI3	-1.8750	-4.1550	455.6347
1006000	ORPIMENT	-82.8900	60.9710	246.0350
1006001	REALGAR	-30.5450	19.7470	106.9855
3006100	AS2O5	5.4050	-6.6990	229.8400
5295000	ZN(BO2)2	0.0000	-8.2900	150.9893
5216000	CD(BO2)2	0.0000	-9.8400	198.0188
5260000	PB(BO2)2	5.8000	-7.6100	292.8093
7047001	MNHPO4(C)	0.0000	25.4000	150.9174
7060006	PBHPO4	0.0000	23.9000	303.1693
7060007	PB3(PO4)2	0.0000	44.5000	811.5125
73100	SULFUR	4.2000	2.1100	32.0640
7203000	ALASO4.2W	0.0000	-4.8000	165.9006
7215000	CA3(ASO4)26W	0.0000	-22.3000	506.1700
7223100	CU3(ASO4)26W	0.0000	-6.1000	576.5680
7228100	FEASO4.2W	0.0000	-0.4000	230.7967
7247000	MN3ASO428W	0.0000	-12.5000	586.7746
7254000	NI3(ASO4)28W	0.0000	-15.7000	459.1707
7260000	PB3(ASO4)2	0.0000	-5.8000	899.4079
7295000	ZN3ASO422.5W	0.0000	-13.6500	518.9862
7210000	BA3(ASO4)2	-2.6400	8.9100	689.8580
90000	V METAL	62.9000	-42.3500	50.9400
2090000	VO	28.0200	-13.0800	66.9390

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	**********	Solid Species	**********	
4190000	VCL2	35.8000	-17.9700	121.8460
3090100	V2O3	19.7200	-4.9000	149.8780
2090100	V(OH)3	0.0000	-7.6500	101.9620
4190100	VCL3	43.9600	-21.7300	157.2990
4190101	VOCL	26.1700	-9.4100	137.8450
3090200	V2O4	14.0700	-4.2700	165.8780
2090200	VO(OH)2	0.0000	-5.8500	100.9540
4290200	VF4	47.5900	-14.9300	126.9320
6090200	VOSO4 (C)	20.7200	-3.5700	162.9970
7090200	(VO)3(PO4)2	0.0000	8.3700	390.7530
4190200	VOCL2	28.2000	-12.7900	137.8450
3090300	V2O5	4.1600	0.7200	181.8770
7315000	TYUYAMUNITE	18.3000	-2.0400	810.0130
7315001	CA-VANADATE	10.1300	-2.8300	237.9560
7315002	CA3(VO4)2	35.0700	-19.4800	350.1150
7315003	CA2V2O7	19.0600	-8.7500	294.0360
7328000	FE-VANADATE	7.3700	1.8600	508.4310
7346000	MG-VANADATE	16.3300	-5.6400	222.1860
7346001	MG2V2O7	30.5000	-13.1800	262.4960
7347000	MN-VANADATE	11.0500	-2.4500	252.8160
7349000	NH4VO3	3.7700	-2.6900	116.9770
7350000	NA-VANADATE	7.0100	-3.7100	121.9280
7350001	NA3VO4	44.4200	-36.9400	183.9080
7350002	NA4V2O7	24.0300	-18.7000	305.8360
7360000	PB3(VO4)2	8.6800	-3.0700	851.4750
7360001	PB2V2O7	3.2200	0.9500	628.2760
7346002	CARNOTITE	8.7000	-0.2300	848.1330
7302000	AG-VANADATE	0.0000	-0.7700	206.8080
7302001	AG2HVO4	0.0000	-1.4800	331.6860
7302002	AG3H2VO5	0.0000	-5.1800	456.5630
4190300	VO2CL	9.6500	-2.8100	118.3920
3090101	V3O5	23.5300	-1.8700	232.8170
3090201	V4O7	39.1500	-7.1400	315.7560
3090202	V6O13	-64.8900	60.8600	513.6320
2015000	LIME	46.2650	-32.7970	56.0800
2015001	PORTLANDITE	30.6900	-22.6750	73.0880
2028000	WUSTITE	24.8460	-11.6870	71.8500
2046001	PERICLASE	36.1350	-21.5100	40.3200
3028001	HERCYNITE	78.3600	-27.1620	173.8100
3046000	SPINEL	89.0890	-36.3330	142.2800
3046001	MAG-FERRITE	66.6390	-16.7650	200.0200
4250000	CRYOLITE	-10.9040	31.4900	209.9530
8215002	WOLLASTONITE	19.4980	-12.9960	116.1700
8215003	P-WOLLSTANIT	21.0680	-13.8460	116.1700

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	**********	Solid Species	**********	
8015001	CA-OLIVINE	54.6950	-37.6490	172.2500
8015002	LARNITE	57.2380	-39.1410	172.2500
8015007	CA3SIO5	106.3350	-73.8670	228.3300
8015003	MONTICELLITE	49.4210	-30.2720	156.4900
8015005	AKERMINITE	76.4450	-47.4720	272.6600
8015004	MERWINITE	107.1110	-68.5430	328.7400
8441000	KALSILITE	28.9190	-12.8380	158.1700
8441001	LEUCITE	22.0850	-6.4230	218.2600
8441002	MICROCLINE	12.3090	-0.6160	378.3500
8441003	H SANIDINE	14.2520	-1.0620	378.3500
8450004	NEPHELINE	33.2040	-14.2180	142.0610
8015006	GEHLENITE	116.1250	-56.8220	374.2100
3028102	LEPIDOCROCIT	0.0000	-1.3710	72.8600
8650000	NA-NONTRONIT	0.0000	14.5040	425.2690
8641002	K-NONTRONITE	0.0000	15.5490	430.5850
8615000	CA-NONTRONIT	0.0000	20.8890	424.3750
8646005	MG-NONTRONIT	0.0000	20.5890	480.6150
87000	Tl metal	-1.2800	-5.6733	204.3700
2087000	Tl2O	23.0550	-27.0984	424.7394
2087001	TlOH	9.9350	-12.9225	221.3773
4187000	TlCl	-10.1370	3.7243	239.8230
4087000	TlBr	-13.6410	5.4190	284.2740
4387000	TlI	-17.2810	7.1964	331.2745
1087000	Tl2S	-21.5600	7.1832	440.8000
6087000	Tl2SO4	-7.9400	3.6942	504.7976
1187000	Tl2Se	-20.3600	6.6848	487.7000
6187000	Tl2SeO4	-9.7600	4.0168	551.6976
5187000	TlNO3	-10.0200	1.5319	266.3749
5087000	Tl2CO3	-8.0200	3.8482	468.7492
2087101	Tl(OH)3	0.0000	6.4503	255.3919
2087100	Avicennite	0.0000	16.3236	456.7382
76000	Se hex,blac	-3.8000	7.6963	78.9600
76001	Se (A)	-2.6000	7.1099	78.9600
1228001	Ferroselite	-11.3000	18.5959	213.7670
1260000	Clausthalit	-28.0000	21.2162	286.1600
1202000	Ag2Se	-64.9500	43.6448	294.6960
1216000	CdSe	-18.1600	18.0739	191.3700
1223100	CuSe	-28.9500	26.5121	142.5060
1223000	Cu2Se alpha	-51.2100	36.0922	206.0520
1223101	CuSe2	-33.6000	33.3655	221.4660
1223001	Cu3Se2	-81.3400	63.4911	348.5580
1228000	FeSe	-0.5000	7.1466	134.8070
1247000	MnSe	13.4600	-5.3508	133.8980
1295000	ZnSe	-6.4390	11.3642	144.3400

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Solid Species	**********	
1220000	CoSe	0.0000	16.2723	137.8932
1254000	NiSe	0.0000	17.7382	137.6600
2076100	SeO2	-0.3350	-0.1246	110.9588
6110000	BaSeO3	6.2800	-4.1634	264.2882
6115000	CaSeO3:2H2O	4.6500	-2.8139	203.0686
6123100	CuSeO3:2H2O	8.8100	-0.4838	226.5346
6128100	Fe2(SeO3)3:	0.0000	20.6262	528.5990
6128101	Fe2(OH)4SeO	0.0000	-1.5539	306.6814
6146000	MgSeO3:6H2O	-1.2500	-4.0314	259.3544
6147001	MnSEO3:2H2O	-2.0300	-0.9822	217.9266
6154000	NiSeO3:2H2O	7.4100	-2.8147	221.6886
6180000	SrSeO3	0.0000	-0.1034	214.5782
6147000	MnSeO3	0.0000	-0.0440	181.8962
6120000	CoSeO3	0.0000	-0.1906	185.8914
6102000	Ag2SeO3	-9.4700	8.1977	342.6942
2076200	SeO3	34.9850	-21.0440	126.9582
6102001	Ag2SeO4	-10.4500	8.9014	358.6936
6110001	BaSeO4	-2.0000	5.1895	280.2876
6115001	CaSeO4:2H2O	-0.8800	2.9473	219.0680
6160000	PbSeO4	-3.8000	6.8387	350.1576
6180001	SrSeO4	-2.6900	6.8747	230.5776
36000	Hg metal (1	-19.9350	13.4552	200.5900
4036000	Hg2Br2	-31.2520	22.2091	560.9880
5036000	Hg2CO3	0.0000	13.9586	461.1892
4136000	Calomel	-23.4440	17.8427	472.0860
4236000	Hg2F2	4.4320	3.0811	439.1768
4336000	Hg2I2	0.0000	28.2782	654.9890
2036000	Hg2(OH)2	0.0000	-5.2603	435.1946
7036000	Hg2HPO4	0.0000	25.9795	497.1593
6036000	Hg2SO4	-0.2300	6.1593	497.2376
6136000	Hg2SeO3	0.0000	6.9290	528.1382
4036100	HgBr2	-34.4520	25.3730	360.3980
5036100	HgCO3	-22.1300	28.6817	260.5992
4136100	HgCl2	-27.2640	21.7858	271.4960
4336100	Coccinite	-49.7320	34.6599	454.3990
2036100	Montroydite	-5.1150	3.6503	216.5894
2036101	Hg(OH)2	0.0000	3.4963	234.6046
1036100	Cinnabar	-60.4300	45.1885	232.6500
1036101	Metacinnaba	-59.5300	44.8220	232.6500
6036100	HgSO4	-3.5100	9.4189	296.6476
6136100	HgSeO3	0.0000	12.6953	327.5482
4336102	HgI2:2NH3	-32.6320	16.1066	488.4598
4336103	HgI2:6NH3	20.5680	-33.8566	556.5814
2021100	CR(OH)2	8.5100	-10.8189	86.0106

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Solid Species	**********	
4021100	CRBR3	33.7770	-19.9086	291.7080
4121100	CRCL3	27.5090	-13.5067	158.3550
4221100	CRF3	4.3630	13.2597	108.9912
4321100	CRI3	32.1270	-20.4767	432.7095
3021100	FECR2O4	24.8600	0.9016	223.8366
3021101	MGCR2O4	39.8600	-12.0796	192.2946
21000	CR METAL	34.3000	-32.2440	51.9960
3021102	CR2O3	12.1250	3.3937	151.9902
2021102	CR(OH)3 (A)	0.0000	0.7500	103.0179
2021101	CR(OH)3 (C)	7.1150	-1.7005	103.0179
4121000	CRCL2	19.6660	-15.8676	122.9020
3021200	AG2CRO4	-14.0400	11.5548	331.7296
3021201	BACRO4	-6.3900	9.6681	253.3236
3021202	CS2CRO4	-7.5040	0.5541	381.8044
3021203	CS2CR2O7	-22.8990	17.7793	481.7986
3021204	CUCRO4	0.0000	5.4754	179.5396
3021205	K2CRO4	-4.2500	-0.0073	194.1902
3021206	K2CR2O7	-18.1250	15.6712	294.1844
3021207	LI2CRO4	10.8220	-4.8568	129.8756
3021208	MGCRO4	21.2600	-5.3801	140.2986
3021209	(NH4)2CRO4	-2.1900	-0.4046	152.0702
3021210	NA2CRO4	4.6100	-3.2618	161.9731
3021211	NA2CR2O7	-5.3050	9.8953	261.9673
3021212	PBCRO4	-10.2300	13.6848	323.1936
3021213	RB2CRO4	-5.8920	0.0968	286.9292
3021214	SRCRO4	2.4200	4.8443	203.6136
2021200	CrO3	1.2450	3.2105	99.9942
3015000	CaCrO4	6.4400	2.2657	156.0736
3036000	Hg2CrO4	0.0000	8.7031	517.1736
3087000	Tl2CrO4	25.3100	12.0136	524.7336
	**********	Redox Couples	**********	
2812800	FE+3/FE+2	-10.0000	13.0320	0.0000
4914920	NO2/NO3	-43.7600	28.5700	0.0000
4904920	NH4/NO3	-187.0550	119.0770	0.0000
600610	ASO3/ASO4	-30.0150	19.4440	0.0000
8908930	U+3/UO2+2	-10.0300	0.4200	0.0000
8918930	U+4/UO2+2	-34.4300	9.2160	0.0000
8928930	UO2+/UO2+2	-3.3000	2.7850	0.0000
4714700	MN+3/MN+2	25.7600	-25.5070	0.0000
2302310	CU+1/CU+2	1.6500	2.7200	0.0000

Species ID Number	Name	Standard Enthalpy of Reaction	Log K	Gram Formula Weight
	**********	Redox Couples	**********	
9009030	V+2/VO2+1	-35.3300	18.3800	0.0000
9019030	V+3/VO2+1	-44.2300	22.6100	0.0000
9029030	VO+2/VO2+1	-29.3200	16.9300	0.0000
7307320	HS-/SO4-2	-60.1400	33.6600	0.0000
8718700	Tl(OH)3/Tl+	0.0000	48.0178	0.0000
7617600	HSeO3-1/HSe	-78.1700	44.8660	0.0000
7627600	SeO4-2/HSe-	-126.3000	81.1850	0.0000
7627610	SeO4/HSeO3	-48.0950	36.3190	0.0000
3613600	Hg(OH)2/Hg2	-63.5900	42.9870	0.0000
2102110	CR+2/CROH)2	-6.3600	-2.9470	0.0000
2122110	CRO4/CROH)2	-103.0000	67.3760	0.0000
	**********	Gas Phases	**********	
3301404	CH4(GAS)	-61.0000	40.1000	16.0432
3301403	CO2(GAS)	-0.5300	18.1600	41.0100
3300021	O2(AQ) SATO	0.0000	-45.5400	31.9988
3300022	O2(AQ) CALC	133.8300	-85.9800	31.9988
8913305	KU6(OH)15+9	0.0000	-17.2290	1683.2845
3300023	O2(GAS)	-34.1570	-20.7800	0.0000
3600001	Hg (g)	-5.2650	7.8708	200.5900
3600002	Hg2 (g)	-13.8700	14.9630	401.1800
3611400	Hg(CH3)2 (g	115.4000	73.7240	230.6594
3601300	HgBr (g)	34.0040	-16.7900	280.4940
3601800	HgCl (g)	40.0980	-20.5000	236.0430
3602700	HgF (g)	60.9160	-32.7200	219.5884
3603800	HgI (g)	25.2640	-11.1500	327.4945
3611300	HgBr2 (g)	-14.3500	18.4700	360.3980
3612700	HgF2 (g)	0.0000	-0.3800	238.5868
3613800	HgI2 (g)	-28.6300	27.2800	454.3990